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Ueber die Prinzipien bei Durchführung von Schiedsanalysen.

Von Prof. Dr. Th. Wilhelm Fresenius, *Wiesbaden*.

Der Verfasser macht im Namen der Fachgruppe für analytische Chemie des Vereins Deutscher Chemiker folgende Vorschläge.

Bei der Beantragung von Schiedsanalysen muss dem Schiedsanalytiker genau mitgeteilt werden, *was* festgestellt werden soll, also:

(1) Welche Bestandteile zu ermitteln sind.

(2) Falls entschieden werden soll, ob die Ware einer bestimmten Gehaltsanforderung entspricht, *diese* Forderung.

(3) Falls zwischen den Parteien eine bestimmte Analysenmethode vereinbart ist, *diese* Methode.

(4) Falls nicht *ein* Muster eingesandt wird, sondern mehrere, ob die Muster vermischt werden sollen, und in welchem Verhältnis.

Weiter ist hinsichtlich der Mitteilung die Ergebnisse anzugeben, an wen Duplikat-Atteste zu senden sind.

Liegen Angaben von beiden Parteien vor, so müssen dieselben übereinstimmen, beziehungsweise der Schiedsanalytiker muss eine übereinstimmende Weisung herbeiführen. Werden nur von einer Seite Angaben über die oben genannten Punkte gemacht, so gelten diese als im Namen beider Parteien abgegeben. Die Verfügung über die eingesandte Probe hat allein der Einsender.

In Bezug auf den oben unter (2) genannten Punkt ist darauf hinzuweisen, dass, je nach der Art des Untersuchungsobjekts (nach seinem Gehalt an zu bestimmender Substanz, resp. nach der Art derselben), ein entsprechender Spielraum für unvermeidliche Analysenabweichungen berücksichtigt werden muss.

Die Wahl der Methode ist vom Schiedsanalytiker nach bestem Wissen zu treffen insoweit sie nicht durch allgemeinen Gebrauch, oder Vereinbarung beider Parteien festgelegt ist. Ist eine bestimmte Methode vorgeschrieben so ist diese (wenn sie nicht nach Lage der Sache selbstverständlich ist) im Attest speziell anzuführen.

Wenn seitens einer Partei das Ergebnis einer Schiedsanalyse als unzutreffend bezeichnet wird, so hat der Schiedsanalytiker den Fall zu prüfen und, falls sich eine offensichtliche Unrichtigkeit ergibt,

diesen Sachverhalt beiden Parteien mitzuteilen. Findet sich eine solche grobe Unrichtigkeit nicht, so kann eine Revision der Analyse nur mit Zustimmung beider Parteien vorgenommen werden.

Anstände hinsichtlich der Analysenmethoden oder Arbeitsweise werden am besten an Material, welches nicht direkt Gegenstand einer Schiedsanalyse ist, ausgetragen.

Hierbei sich ergebende Abänderungen eingebürgerter Methoden sind zu veröffentlichen, damit die Parteien wissen, welche Art von Resultaten sie zu erwarten haben.

[Von die Vorschläge des Verfassers sind ausführlich publiziert in der "Zeitschrift für angewandte Chemie," *22*, 577 (1909).]

[Die Vorschläge des Verfassers sind ausführlich publiziert in der Schlusssitzung der Sektion I. von dieser gebilligt und dem Kongress zur Genehmigung vorgeschlagen. Eine Beschlussfassung über diesen und alle ähnlichen Vorschläge kam in der letzten Plenarsitzung des Kongresses nicht zu Stande.

A. Friedmann, Györ:—"Auch in dem Falle wenn bei Schiedsanalysen die Methoden nicht vorgeschrieben sind, soll mit dem Resultat die angewendete Methode mitgetheilt werden."

Ueber die Verwendung des Nickeldicyandiamidins in der quantitativen Analyse.

Von Dr. H. Grossmann.

Seit der Entdeckung des Nickeldicyandiamidins, $Ni(C_2H_5N_4O)_2$ durch H. Grossmann und B. Schuch (1907) ist die Methode der Nickelbestimmung und Trennung dieses Elements von anderen Metallen mit Hilfe von Dicyandiaminsulfat (Grossmanns Reagens) in alkalischer Lösung ständig verbessert worden, so dass heute die leicht ausführbare gewichtsanalytische Nickelbestimmung als $Ni(C_2H_5N_4O)_2$ zu den exaktesten analytischen Methoden gerechnet werden darf, wie auch eine kritische Prüfung derselben durch Dr. Prettner (Chem.-Ztg. 1909, ▼▼) kürzlich ergeben hat. In Form von Nickeldicyandiamidin lässt sich Nickel scharf und leicht von den folgenden Elementen der Schwefelammoniumgruppe trennen:

Kobalt, Zink, Eisen, Aluminium, Chrom, Mangan, Molybdän, Wolfram und Uran, sowie den seltenen Erdmetallen. Da $Ni(C_2H_5N_4O)_2$ in wässerigem Ammoniak und Alkalilauge unlöslich ist, so muss man die gleichzeitige Ausfällung der durch die Reagenzien ebenfalls fällbaren Metallhydroxyde durch Hinzufügung einer organischen Hydroxylverbindung verhindern. Es wurden zu diesem Zwecke mit grossem Vorteil bei den einzelnen Trennungen vor allem benutzt: Weinsäure, Citronensäure, Rohrzucker. Die Dicyandiamidinmethode gestattet ferner auch eine glatte Trennung und primäre Abscheidung des Nickels von folgenden Gliedern der Schwefelwasserstoffgruppe: As, Sn, Sb, Pb, Bi, Cd. An Stelle der gewichtsanalytischen Nickelbestimmung kann man aber auch in sehr vielen Fällen, z. B. bei der Analyse von Nickelstählen, die hervorragende massanalytische Cyankaliummethode von Moore resp. Campbell und Andrews benutzen. Dieses in Deutschland immer noch zu wenig bekannte Verfahren lässt sich aber in sehr zweckmässiger Weise mit der Dicyandiamidinnickelmethode kombinieren, wodurch man sehr viel Zeit spart. Man bringt nämlich das gefällte $Ni(C_2H_5N_4O)_2$ nicht, wie früher beschrieben, auf einen Goochtiegel zur Wägung, sondern löst vielmehr den auf einen gewöhnlichen Papierfilter abfiltrierten Niederschlag in verd. HCl, macht schwach ammoniakalisch und titriert nach Moore's Vorschrift mit Cyankalium unter Verwendung von Silberjodid als Indicator. Bei Gegenwart von Kobalt, dessen Menge bis 10 % der vorhandenen Nickelmenge betragen darf, findet man durch direkte Titration, ohne vorherige Abscheidung des Nickels, den Gesamtgehalt Nickel + Kobalt. Bei höherem Kobaltgehalt muss stets die vorherige Abscheidung des Nickels als $Ni(C_2H_5N_4O)_2$ erfolgen, da in solchen Fällen die Oxydation der kobalthaltigen cyankalischen Lösungen exakte Resultate verhindert. Deutsches Walznickel mit ca. 1,5 % Kobalt lässt sich demnach direkt mit Cyankalium titrieren, nicht aber kobaltreiche Erze. Als absolut kobaltfrei erwies sich das Handelsnickel der Mond Nickel Company, das, abgesehen von einem Kohlenstoffgehalt von 0,18 %, nur sehr geringe Verunreinigungen an Eisen enthielt. Die direkte gravimetrische Bestimmung des Nickels als $Ni(C_2H_5N_4O)_2$ ergab in solchem Nickel 99,72 % Ni, die massanalytische 99,77 % Ni. Die einzelnen Trennungsmethoden des Nickels von dem genannten Elemente finden sich in der Dissertation der Herren Heilborn und Hölter beschrieben und werden demnächst auch an allgemein zugänglicher Stelle veröffentlicht werden.

On the detection and estimation of minute amounts of silver, and the solubility of sparingly soluble silver salts.

By George Stafford Whitby.

In addition to its interest in other directions, the estimation of minute quantities of silver in solution is of particular interest at the present juncture when much important work on the determination of atomic weights is proceeding—work of such an order of accuracy that the amount of silver chloride dissolved by cold water necessitates a correction which is reckoned as comparatively large.

A solution of a silver salt, when heated with a little sodium hydroxide and one of a variety of organic bodies, develops a brown or yellow colour even when the amount of silver present is very minute indeed. 50 c.c. of a solution containing one part of silver in 25,000,000 parts of solution give a distinct colour when the procedure described below is followed. If the 50 c.c. of solution taken for the test contain more than ·000025 gms. silver, the colour developed is deep enough to be recognised without its being necessary to transfer the liquid to a Nessler glass; and with still larger amounts of silver a very deep colour may be produced.

The organic substances which have hitherto been found capable of giving this colour when heated with silver solutions containing a little sodium hydroxide are such bodies as dextrine, gum arabic, glycerine, cellulose (in the shape of filter paper), starch, and cane sugar. The method can be extended to the quantitative estimation of minute amounts of silver, since the intensity of the colour produced in a solution is exactly proportional to the silver present.

The routine is as follows: The silver solution is appropriately diluted, and to 50 c.c. are added a few drops of a fairly concentrated solution of cane sugar. The 150 c.c. beaker containing the liquid is immersed in a bath of boiling water for two minutes, about six drops of a normal solution of sodium hydroxide are added, and the heating is continued for 20—30 seconds after the colour has appeared, but for not more than two minutes altogether, since, if no colour has developed after that time, silver may be considered to be absent. The

solution is cooled, transferred to a Nessler glass, and the intensity of the yellow colour determined by noting the number of c.c. of a standard colour of approximately the same intensity, diluted to mark, which it is necessary to place in another Nessler glass in order to match the experimental colour. The most convenient standard colour is one prepared from 5 c.c. of a silver nitrate solution containing ·00001 gms. of silver per c.c. diluted to 50 c.c. 1 c.c. of this standard = ·000001 gms. silver. The standard should be prepared on the same day as that on which the actual determination in which it is to be used is performed, since it sometimes deepens somewhat on standing. By this procedure it is possible to estimate ·000002 gms. of silver in 50 c.c. of solution, *i.e.*, ·00004 gms. of silver per litre.

The method should prove of value in correcting for the solubility of silver halides in water in accurate gravimetric work, such as the determination of atomic weights. It is of about the same degree of delicacy as the nephelometric method described by Richards and Wells (Amer. Chem. Jour., 1904, 31, 235). It is, however, much easier and quicker in execution, and is free from complications. To judge by the statements made by Richards and Wells (Jour. Amer. Chem. Soc., 1905, 27, 498), it could probably be applied even if the precipitate were washed with silver nitrate solution according to Richards' procedure, since it is only after the silver nitrate has been washed out, as indicated by the absence of nitrate in the wash-waters, that any appreciable amount of silver chloride is dissolved by the wash-water.

In conducting the method of estimating silver here described, ammonia must not be present; but, as regards the presence of metals other than silver, quantities of copper, zinc, mercurous, mercuric, bismuth, cadmium, and lead of the same order as the silver present, *i.e.*, quantities insufficient to give an appreciable precipitate with sodium hydroxide, do not interfere with the development of the colour. In the case of lead, the precipitate from which will dissolve in an excess of sodium hydroxide, it was found that, even when the lead present in the solution was 8,000 times the silver present, the colour developed. This matter is being investigated further.

An explanation of the mechanism of the action by which the colour is produced can be given. The colour obtained as above by the action of one of the various organic substances mentioned and sodium hydroxide on solutions of silver salts is due to the presence

of colloidal silver. The solutions give the Tyndall effect, are precipitated by small quantities of hydrochloric acid, and display the other characteristics of colloidal solutions of silver. Further, a solution of silver oxide develop the yellow colour when boiled with cane sugar alone without its being necessary to add sodium hydroxide. But no other silver salt behaves in this way; the others all require the presence of sodium hydroxide in order to give the colour. It would thus appear that the sodium hydroxide acts on the silver salt to produce silver hydroxide, which then reacts directly with the organic substance. All the organic bodies used are carbohydrates or hydroxy compounds, and the probability is that a hydrogen ion is split off from the organic molecule, receives the charge from the silver ion, and combines with the hydroxyl ion of the silver hydroxide to form unionised water. The silver, relieved of its ionic charge, goes into colloidal solution.

In agreement with this idea are the facts that other alkalies, such as baryta water, can take the place of sodium hydroxide, and that the sodium hydroxide is not a catalyst in this reaction, since a certain minimal quantity, namely, the amount corresponding to silver in the solution, must be present, in order that the full colour may develop.

The accurate determinations of the solubilities of "insoluble" and sparingly soluble silver salts have hitherto been made almost entirely by physical methods, particularly by the conductivity method introduced by Kohlrausch. But the method of estimating minute amounts of silver described in this communication makes it possible to determine the solubility of sparingly soluble silver salts by a chemical method. It may be said that, in general, the results obtained confirm those arrived at by physical means.

The method here used has certain distinct advantages over the conductivity method. It is altogether more rapid and simple in execution, and suffers from the presence of no disturbing factors—particularly, it is not affected by the presence of other electrolytes in solution, but takes account only of the silver in solution.

The results obtained are recorded in the table. The following, however, require comment:—

Chloride.—The freshly-prepared powdery variety was used, and the result for its solubility in cold water agrees with the value decided upon by Kohlrausch in his summary of the solubility of "insoluble" salts as determined by the conductivity method. The

earlier results obtained by the conductivity method are very discordant.

The value of the solubility of silver chloride in water at 100° serves again to emphasise the danger of precipitating this substance in boiling water and washing it with boiling water in gravimetric work having any great pretensions to accuracy.

Silver chloride is very soluble in concentrated hydrochloric acid, but its solubility in dilute hydrochloric acid has not been previously recorded. The following results conform to the expectations of the ionic theory. When the quantity of hydrochloric acid amounts to only 1 per cent., the access of chlorine-ions diminishes the solubility. As the acid present increases this tendency is overcome by the considerable solubility of silver chloride in hydrochloric acid, so that when it amounts to 5 per cent. the solubility is greater than that in water.

At 21° 1 per cent. hydrochloric acid dissolves ·0002 gms. Ag. per litre.

At 21° 5 per cent. hydrochloric acid dissolves ·0033 gms. Ag. per litre.

At 21° 10 per cent. hydrochloric acid dissolves ·0555 gms. Ag. per litre.

Chromate.—The results show that the solubility does not decrease with increase of temperature as is indicated by the value given by Abegg and Cox. The value given for the solubility of silver chromate at 27° was confirmed, through the medium of the colour given to the solution by the chromate ion, by use of a standard solution of potassium chromate.

Oxide.—The amount of silver oxide dissolved by water was found to change on allowing the solution to stand in contact with the solid. Initially ·0172 gms. per litre, it gradually increased, reached a maximum of approximately twice its original value in the course of about five days, then fell, and, after about fourteen days' standing, became constant at ·0215 gms. The results previously recorded have been of a discordant nature, varying from ·081 to ·0174 gms. per litre. The above observation largely explains the disagreement. The result obtained agrees with that arrived at by the latest observer, Böttger, who found that it was necessary to stir the liquid containing the silver oxide in order to get constant readings.

SOLUBILITIES OF SPARINGLY SOLUBLE SILVER SALTS IN WATER.

Salt.	Temperature.	Grams per litre.	Other observers.	Temperature.	Grams per litre.	Method.
Arsenate	20°	·0085				
Arsenite	20°	·0115				
Bromate	27°	1·71	Longi[1]	25°	1·66	
			A. A. Noyes[2]	25°	1·91	Direct.
			Böttger	20°	1·586	Conductivity.
Carbonate ...	25°	·0523	Abegg and Cox[4] ...	25°	·033	Nernst's potential formula.
Chloride	21°	·00154	Kohlrausch and others[5]..	20°	·00160	Conductivity.
			Böttger[8]	20°	·00153	,,
	100°	·0217	,, [6]	100°	·0218	,,
Chromate ...	18°	·0256	Kohlrausch and Rose[7]...	18°	·026	,,
	27°	·0341	Abegg and Cox[4] ...	25°	·020	,,
	50°	·0534				
Ferricyanide ...	20°	·00066				
Iodate	20°	·039	Kohlrausch[5]	18°	·040	,,
			Böttger[8]	20°	·0435	,,
Oxalate	21°	·0378	,, ...	20°	·0365	,,
Oxide	20°	·0215	,, ...	20°	·0214	,,
Thiocyanate ...	21°	·00025	Abegg and Cox[4] ...	25°	·0002	,,
			Kuster and Thisle[8] ...	25°	·00017	Nernst's potential formula.
			Böttger[8]	20°	·00014	Conductivity.

[1] *Gazzetta*, 13, 87, 1883. [2] *Zeit. Physikal. Chem.*, 1890, 6, 246. [3] *Ibid.*, 1903, 46, 602. [4] *Ibid.*, 1903, 46, 11.
[5] *Ibid.*, 50, 356. [6] *Ibid.*, 56, 82. [7] *Ibid.* 1893, 12, 241. [8] Zeit. anorg Chem., 1903, 33, 139.

La Determinazione Volumetrica dell' Argento col Metodo di Gay Lussac.

Nota di E. Pannain.

Il metodo, adottato nelle Zecche e negli uffici del saggio dei metalli preziosi per titolare le leghe di argento, è quello classico proposto dal Gay Lussac.

La lega viene disciolta in acido nitrico, e l' argento, in essa contenuto, vien precipitato mediante una quantità determinata di una soluzione titolata di cloruro sodico; la fine della reazione si riconosce dal fatto che tanto una soluzione di cloruro di sodio quanto una soluzione di nitrato di argento, versate nel liquido reso limpido per agitazione o per filtrazione, non producono intorbidamento, ma solo una leggera opalescenza sulla superficie del liquido limpido. Questa opalescenza detta "conferma" sparisce, quando si rimescola il liquido, senza però intorbidarlo.

La soluzione titolata di cloruro di sodio, che prende il nome di "soluzione normale," contiene in 100 gr. od in 100 cc. la quantità di sale necessaria per precipitare completamente un grammo di argento puro. E che sia tale si prova mediante una soluzione dieci volte più debole, detta "soluzione decima", di cui un cc. corrisponde ad un mg. di argento. Si scioglie un gr. di argento chimicamente puro in dieci cc. di acido nitrico a 32°Bé, e vi si aggiungono i 100 gr. o i 100 cc. della soluzione normale. Un cmc della soluzione decima, versato lentamente in modo che non si mescoli col liquido limpido, dal quale si è separato il cloruro di argento, deve appunto produrre la conferma.

Per la rapidità e l' esattezza delle operazioni, in luogo di filtrare, il Gay Lussac propose, e così si è sempre fatto, di eseguire il saggio in una boccetta da 150-200 cc. con tappo smerigliato a perfetta tenuta. Versata la soluzione normale sulla soluzione della lega di argento in acido nitrico, basta agitare per quattro o cinque minuti, perchè tutto il cloruro di argento si raccolga sul fondo della boccetta, ed il liquido resti perfettamente limpido.

Questa operazione per rendere limpido il liquido è molto noiosa ed è anche lunga, specialmente quando è necessario aggiungere parecchi cc. di soluzione decima prima di arrivare alla conferma,

tanto più che, dopo l' aggiunta di alcuni cc. di soluzione decima di cloruro di sodio o di nitrato di argento, riesce più difficile rendere limpido il liquido sottoposto all' analisi. Nè giova ad abbreviare l' operazione l' agitazione meccanica, perchè, se è vero che si possono agitare più boccette contemporaneamente, la durata di ogni agitazione è maggiore che se si agita a mano.

Per rendere limpida la soluzione, mi servo con vantaggio di un apparecchio per filtrare assai semplice, che rende molto sollecito il processo analitico, sopprimendo la noiosa agitazione, senza complicazione alcuna.

L' apparecchio è costituito da un tubo di vetro a pareti ben trasparenti lungo 8-10 cm. e del diametro di circa 3 cm., che nella parte inferiore si restringe in un altro più sottile del diametro di 4-5 mm., lungo 20-25 cm., e che, passando attraverso un tappo a due fori, va a pescare nel liquido da filtrare. A qualche centimetro dal tubo largo quello stretto porta un rigonfiamento per la lunghezza di 2 o 3 cm., nel quale vi è uno strato di amianto, tra due di lana di vetro ben compressi in modo da formare un filtro perfetto. Corrispondentemente al principio ed alla fine di questo filtro, partono due tubi laterali riuniti tra loro mediante un rubinetto. Collocato l' apparecchio in modo che l' estremo inferiore peschi nel liquido da filtrare, si chiude il rubinetto e si applica al tubo superiore un tappo forato, attraverso il quale passa un tubo di vetro collegato ad una pompa aspirante, per mezzo della quale si fa il vuoto ed il liquido filtra attraverso la lana di vetro e l' amianto, e passa perfettamente limpido nel tubo largo, nel quale se ne fa raccogliere fino a farlo riempire per metà circa. Quindi, interrotta l'aspirazione e tolto il tappo, vi si versa lentamente la soluzione decima di cloruro di sodio, evitando che si mescoli con quella filtrata e si osserva se si ha la conferma, oppure se il liquido contiene un eccesso di argento o di cloro; in questi due ultimi casi si apre il rubinetto e il liquido passa rapidamente nel recipiente, si lavano le pareti interne del tubo superiore e si fanno passare anche le acque di lavaggio attraverso il rubinetto di vetro; se è necessario si versano nel liquido altri cc. di soluzione decima di cloruro di sodio o di altra equivalente di nitrato di argento, si agita e si filtra di nuovo, e si continua come prima fino ad ottenere la conferma.

Questo piccolo apparecchio è preferibile a quelli proposti per filtrare liquidi nei quali si è precipitato il solfato di bario o altri

sali insolubili,* perchè permette che il liquido ritorni nel primitivo recipiente, senza passare di nuovo attraverso gli strati filtranti, evitando una ulteriore aspirazione o compressione, che lascerebbe al disopra degli strati filtranti parti solide, che, nelle successive filtrazioni, intorbiderebbero il liquido che va nel tubo superiore.

Per eseguire il saggio di una lega di argento, la misura della soluzione titolata di cloruro di sodio si può fare a peso od a volume, a seconda che la soluzione normale, che si è preparata, è tale che 100 gr. o 100 cc. equivalgano ad un gr. di argento puro.

Versato il peso od il volume della soluzione normale sulla soluzione della lega in acido nitrico, l' analisi si continua nello stesso modo in ambo i casi, mediante la soluzione decima fino ad ottenere la conferma.

I due metodi a peso ed a volume differiscono fra loro unicamente per il modo di misurare la soluzione normale. Poichè 100 gr. della soluzione normale a peso precipitano esattamente un grammo di argento puro, un cg. equivale ad un decimo di mg.; quindi basta che la pesata sia approssimata al mezzo cg. perchè l' errore sia inferiore ad un decimo di millesimo. Per ottenere la medesima esattezza col metodo a volume è necessario che l' errore di misura del volume del liquido sia inferiore ad un centisimo di cc.; e difatti è così: prelevando con la medesima pipetta a riempimento completo più volumi di 100 cc. della stessa soluzione alla medesima temperatura, nelle identiche condizioni, ho avuto differenze di 5 mg. in più o in meno.

Sia dunque che il saggio si esegua a peso od a volume, l' errore dipendente dalla misura della soluzione normale è compreso nei medesimi limiti, e poichè i lue metodi differiscono solo nel diverso modo di determinare la quantità di soluzione normale necessaria per il saggio, può dirsi che entrambi offrono lo stesso grado di approssimazione.

Sta però il fatto che una soluzione normale, preparata in modo che 100 gr. contengano tanto cloruro di sodio da precipitare esattamente un grammo di argento puro, si conserva tale qualunque variazione di temperatura abbia luogo, mentre una soluzione normale, che contenga in 100 cc. tanto cloruro di sodio quanto basta per precipitare esattamente un gr. di argento puro, varia di titolo al variare della temperatura.

* Tarugi e Bianchi, Gazzetta Chimica It. 1906, XXXVI, p. 347; Lang e Allen, Jour. Ch. Soc. London 91, II., p. 1370.

Essendo stata calcolata la differenza di titolo, che subisce una soluzione normale preparata ad una data temperatura quando viene portata a temperatura diversa, l' errore dovuto alla variazione della temperatura si può compensare mediante correzione.

Il metodo a peso presenta dunque il vantaggio che il titolo della soluzione è indipendente della temperatura: la sua precisione è collegata solo alla bontà della bilancia, ma le manipolazoni sono molto delicate e richiedono lungo tempo, specie per la pesata. Il metodo a volume richiede una correzione per la variazione di temperatura e la sua esattezza è collegata alla scrupolosità con cui si esegue l' analisi, ma è preciso quanto quello a peso, è più rapido ed è di facile esecuzione.

Cosicchè, quando si devono eseguire numerosi saggi, è ad esso che va data la preferenza, lasciando quello a peso per i casi di contestazione in cui l' analista vuol dare un risultato, che non dipenda assolutamente dalla sua personale abilità, ma dall' esattezza degli strumenti che adopera.

L' errore massimo che si può commettere può essere di ±0,15 mmi. Esso è dovuto per una parte alla differenza fra la quantità di soluzione titolata prelevata per il saggio e quella che realmente corrisponde ad un grammo di argento (errore di misura) e che ascendo a ±0,05 mmi., e per un' altra parte alla precisione della pesata della lega per circa ± 0,05 mmi., ed in fine alla sensibilità dell' apprezzamento della fine della reazione, e, poichè il cloruro di sodio permette di riconoscere meno di mezzo decimo di mg. di argento in una soluzione di 120-150 cc., anche questa terza causa può determinare un errore di ± 0,05 mmi.

Operando con molta scrupolosità l' errore può essere diminuito e si possono ottenere risultati straordinariamente precisi, per reciproca compensazione delle diverse cause di errore.

Cercando la conferma con una soluzione decima il titolo della lega si può avere approssimato fino al millesimo, la pratica però consiglia di dare alla conferma un certo valore, con una approssimazione di due decimi di millesimo con una soluzione centesima si approssima fino al decimo di millesimo.

Sia che il saggio si esegua a peso, sia a volume, la precisione del risultato dipende non solo dal rigore con cui si determinano il peso ed il volume della soluzione normale, ma ancora dal seguire, tanto nella titolazione della soluzione normale quanto nell' esecuzione del saggio, sempre le medesime norme, in modo da trovarsi nelle

medesime condizioni, e procedendo con la massima rapidità, (al quale scopo riesce veramente opportuno l' apparecchino a filtrare di cui mi servo), procurando di aggiungere il minor numero possibile di cc. di soluzione decima per arrivare alla conferma.

Nell' eseguire il saggio si deve tener conto della intensità della conferma e della rapidità con la quale essa si forma. Al riguardo la pratica fornisce il miglior insegnamento; è consigliabile però di eseguire sempre un saggio testimone con argento a mille all' inizio di ogni serie di analisi, ottenendosi così il titolo preciso dell' acqua normale ed una norma sicura per il riconoscimento della conferma non solo per il saggio a volume, nel qual caso si elimina ogni correzione dipendente da variazioni di temperatura, ma anche per quello a peso, giacchè la temperatura alla quale si opera ha grande influenza sulla rapidità di formazione della conferma. Una giusta conferma deve cominciare a palesarsi non appena si è finito di versare la soluzione decima o centesima e non deve diffondersi nel liquido per oltre tre o quattro millimetri dopo 4 o 5 minuti, ma deve abbassarsi per poi sparire, dopo un tempo più lungo.

Dr. E. P. Perman read a Paper on

Apparatus for the Absorption of Gases.

Nouveaux Documents sur le dosage du bore.

Par H. Copaux et G. Boiteau.

Les auteurs ont étudié le dosage du bore et recherché quelle est la plus exacte des méthodes actuellement usitées, à savoir : l'épuisement par l'éther, l'entraînement par l'alcool méthylique et le titrage acidimétrique en présence de glycérine.

Ils donnent la préférence au dernier procédé, qui s'est montré commode et précis, méme dans les cas difficiles, comme l'analyse des borures et des borotungstates.

Les resultats suivants ont été obtenus :—

Borures.

Borure de fer.	Borure de nickel.	Borure de cobalt.	Borure de chrome.
Bo- 8,65	Bo- 7,01	Bo- 8,21	Bo-16,19
Fe-90,75	Ni-92,10	Co-91,12	Cr-84,10
	Fe- 1,19		
99,40	100,30	99,33	100,29

Borotungstates.

1°. Mélanges synthétiques de 1 gr. TuO^4Na^2 $2H^2O$ avec de l'acide borique.

BO^3H^3	Trouvé.
0,0186	0,0182
0,0258	0,0258
0,0451	0,0450
0,1666	0,1670

2° Acides borotungstiques.

	Acide hexagonal.		Acide quadratique.	
	Moyenne de 3 analyses.	Calculé pour B^2O^3 $28\,TuO^3$ $62\,H^2O$.	Moyenne de 3 analyses.	Calculé pour B^2O^3 $24\,TuO^3$ $66\,H^2O$.
B^2O^3	0,94	0,91	1,0	1,02
TuO^3	84,31	84,57	81,45	81,58
H^2O	14,52	14,52	17,38	17,40
	99,77	100,0	99,83	100,0

Procédé rapide de dosage du Vanadium dans les Minéraux et les Produits Industriels Vanadifères.

Par le Prof. Piñerúa y Alvarez,

Laboratoire d'analyse chimique spéciale de la Faculté des Sciences de Madrid.

La détermination quantitative ou évaluation du vanadium dans les minéraux et autres produits industriels (ex. *les alliages ferrovanadifères*) a été l'objet d'incessantes études depuis Berzelius et Rose jusqu'à nos jours par Gerland, Goldschmidt, Roscoe, Norblad, Gooch et Gilbert, Gooch et Stockey, Hillebrand, Browning, Truchot, Maillard, Levisato, Hauser et beaucoup d'autres chimistes.

Quelques-uns des procédés imaginés sont très recommandables, mais nous croyons que le nôtre emporte l'avantage quant à la rapidité et à l'exactitude. On peut aussi l'appliquer avec de légères variations à l'évaluation du molybdène et du tungstène ou wolframium dans leurs minerais ou produits métallurgiques.

Le procédé consiste à fondre le minerai porphyrisé ou le matériel vanadifère réduit en poudre très fine (0·5 gr. à 1 gr.) avec sept ou huit fois son poids de *bioxyde de sodium* très sec et pur en maintenant le mélange en fusion à la température du rouge pendant quinze ou vingt minutes.

Une fois la masse refroidie on la soumet à l'action de l'eau bouillante et on sépare le résidu insoluble au moyen de filtration en le lavant soigneusement sur un filtre.

Le filtré alcalin s'acidifie avec SO_4H_2, puis on ajoute de l'alcool, et sans séparer le précipité—s'il y en a—on fait passer par le liquide un courant d'anhydride sulfureux jusqu'à ce qu'il ait une forte odeur de ce gaz.

Il est convenable de prolonger l'action du gaz réducteur pendant assez de temps, surtout si le matériel analysé contient de l'arsenic.

Ensuite, on filtre—s'il est besoin—le liquide *bleu* qui résulte et on élimine, par la chaleur, l'alcool et le gaz sulfureux qu'il renferme dissous en favorisant, à la fin, l'expulsion de ce gaz au moyen d'un courant d'anhydride carbonique.

Si le minerai ou le matériel vanadifère contient de l'arsenic,

comme par exemple l'*endlichite,** la *chiléite,*† l'*aréoxène,*‡ l'*eusynchite*§ et le *chloro-arsenio-vanadate de plomb* de Santá Marta (mine *Clemente*) * de la province de Badajoz (Espagne), on soumet de nouveau le liquide *bleu*, après avoir expulsé le gaz sulfureux, à un courant d'hydrogène sulfuré, tandis que se forme le precipité jaune de trisulfure d'arsenic.‖

Celui-ci est séparé par filtration. On élimine le gaz sulfhydrique en faisant bouillir le liquide et enfin on évalue par titrimétrie le vanadium de la solution bleue au moyen du permanganate potassique en solution à 1 %, en la titrant avec une autre également à 1 % de métavanadate d'ammonique bouillie avec de la lessive de soude jusqu'à ce qu'elle ne dégage plus d'ammoniaque ; on la réduit par le gaz sulfureux après l'avoir acidifiée fortement avec SO_4H_2 en opérant à chaud et dans les mêmes conditions de concentration, d'acidité et de température qu'avec le matériel analysé ; on termine l'évaluation titrimétrique quand le liquide bleu se décolore, à cause de la transformation du sel hypovanadique en vanadique et celui-ci acquiert une légère teinte rose permanente.

En procédant comme nous l'avons indiqué on obtient des résultats très exacts dans beaucoup moins de temps qu'avec d'autres procédés.

En travaillant sur la *vanadite* de Santa Marta nous avons trouvé une quantité d'arsenic à l'état d'orthoarséniate qui coïncide presque exactement avec celle qui correspond à la formule

$$(VaO_4)_2\,(AsO_4)\,Pb_4\,(ClPb)\,;$$

de façon que l'on doit la considérer comme un *chlorarsénivanadate-o- de plomb.*

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* *Genth* et *Collie*, J. prakt. Chem. Soc., *55*, 94, 1899.

† *Domeyko*, An. Min., *74*, 150, 1848.

‡ *Bergemann*, Jahrbuch Mineral., *397*, 1857.

§ *Rammelsberg*, Sitz. preuss. Akad., *40*, 1864.

‖ La quantité d'arsenic trouvée a été de 5·24%.

Nachträgliche Bemerkungen zur Zellulosebestimmung.

Von C. Councler.

Damit eine Methode quantitativer Zellulosebestimmung wirklich brauchbar sei, muss sie einen Rückstand ergeben, der nicht nur qualitativ die Reaktionen, sondern genügend genau auch die quantitative Zusammensetzung der Zellulose zeigt, auch muss die Zellulose vollständig oder nur mit vernachlässigbarem Verluste wirklich zur Wägung herausgebracht werden. Nur zwei der bisherigen Methoden genügen diesen Anforderungen, leider sind aber beide nach anderer Richtung nicht ganz einwurfsfrei. Es sind die von Cross und Bevan und die von Hugo Müller. Damit eine Messmethode wissenschaftlich brauchbar sei, müssen die bei den Bestimmungen unvermeidlichen Differenzen "kleine Grössen" im Sinne der Mathematik sein, d.h. Grössen, die als Summanden neben einem *viel* grösseren Posten auftreten, dessen Bestimmung nicht *so* genau möglich oder nötig ist, dass jener andre Posten, die kleine Grösse, überhaupt noch in Betracht käme.

Das erfüllt am besten Müller's Methode. Ich habe alle von mir angegebenen Analysen (s. "Compte rendu") persönlich ausgeführt, folgende sechs unter Anwendung einer Lupe, um auch nicht *eine* Faser zu verlieren. Dabei erhielt ich (Brauner Holzschliff, für Trockensubstanz) Prozente Zellulose: 58·69; 58·94; 58·96; 58·94; 58·96. Hier sind die Differenzen klein. Bei der Analyse nach Cross u. B. dagegen kommen, wie ich nach mehrjähriger Erfahrung behaupten darf, Differenzen von 2–4 % nicht selten, gelegentlich aber noch höhere vor, bezw. solche Fehler, die nicht mehr "kleine Grössen" sind.

Trotzdem wird für die *Rohmaterialien* (Holz und Holzschliff) bis auf weiteres nach Cross analysiert werden müssen, da bei dieser Methode das Ziel am raschesten erreicht wird. Dagegen bin ich bezüglich der reineren Zellulosen unbedingt für H. Müller's Methode, weil jedes andere Verfahren namentlich den Gehalt der allerbesten Zellulosen zu niedrig finden lässt.

Denn: in diesen wird die Zellulose unzweifelhaft von der 1%-igen Natronlauge, welche Cross anwendet, angegriffen. Die Cross'sche Methode ist sehr gut für fein gepulvertes oder zerhobeltes

Eichen- oder Quebrachoholz, bei denen der Gerbstoff einen merklichen Teil des Natrons neutralisiert, nicht aber für die sehr reinen, durch ein *Reduktionsmittel* wie Kalziumbisulfit erzeugten Zellulosen. Also: für wirkliche Zellulosen empfehle ich H. Müller's Verfahren, das übrigens auch gerade bei diesen sehr rasch, meist in nicht ganz zwei Tagen, zum Ziele führt.

Um übereinstimmende Resultate zu bekommen, muss man auch hier die Punkte, auf welche es ankommt, genau *festsetzen*. Dringend empfehle ich:

(1) immer bei 105° oder im Vakuum zur Konstanz zu trocknen, sowohl das Ausgangsmaterial wie die resultierende Zellulose;

(2) im übrigen die von Cross bezw. H. Müller gegebenen Vorschriften genauest zu befolgen, nur dass

(3) beim Cross-Verfahren Filtration *durch* ein *Papierfilter* auf dem Goochtiegel gestattet wird (statt durch Leinen);

(4) die Asche der erhaltenen Zellulose jedesmal zu bestimmen und abzuziehen.

PERCY H. WALKER read a Paper on

The Contracts Laboratory of the Bureau of Chemistry.

Nota al Metodo Goldemberg e Geromont per l'analisi delle materie tartariche.

Dottor. OSCAR TOBLER e Dr. R. CARAMELLI.

Abbiamo avuto occasione di dover studiare le modificazioni apportate al Metodo Goldemberg 1898, già proposte dalla commissione internazionale d'analisi al precedente congresso di Chimica applicata, tenuto in Roma l'anno 1906 e publicate anche nello Zeitschrift für Analytische Chemie (erstes Heft 1908, Seite 57) sotto il titolo di metodo 1907. A nostro avviso ci sembra più esatta la prescrizione 1898 dove dice che dopo il trattamento all'ebolizione con Carbonato Potassico si debba eseguire la filtrazione e il lavaggio di tutta la massa, mentre il metodo modificato prescrivendo di spruzzare la massa stessa in un pallone da 200 c.c. e dopo raffreddamento portare fino a segno, filtrare e del filtrato prendere c.c. 100 non tiene nessun conto del deposito di Carbonato di Calcio che entra a far parte dei 200 c.c. per cui i 100 c.c. non possono rappresentare esattamente la metà del liquido, come dovrebbe essere, bensì un eccesso che sarà direttamente proporzionale alla quantità di Calcio contenuta nella materia da analizzare. E questo eccesso l'abbiamo voluto praticamente comprovare coi seguenti esperimenti tipici:

I.—Miscela di gr. 3,4 di acido tartarico $\frac{1}{2}$ gr. 2,6 di CaO. = gr. 6 dal titolo calcolato 56,6 %.

Trovato	Metodo 1907	... ...	57,8 %
	id. 1898	... ...	56,6 %

II.—Tartrato di calce 98,1 purezza = 56,6 % in a.t.

Trovato	Metodo 1907	... ...	57,2
	id. 1898	... ...	56,6

III.—Tartrato di calcio preparato dalle acque nere nella lavorazione dell' Acido Tartarico.

Trovato	Metodo 1907	... ...	39,4 %
	id. 1898	... ...	38,0 %

IV.—Miscela in parti eguali di Tartrato a 56,6 % e Cremore purissimo.

Titolo calc. 68,1 % a.t.

Trovato	Metodo 1907	... ...	68,4 %
	id. 1898	... ...	68,0 %

V.—Limo di 52,4 acidità totale miscela di gr. 5 + gr. 1 CaO.

Titolo calcolato	...	43,6 % a.t.
Trovoto 1907	...	44,2 % a.t.

VI.—Stesso Limo miscela di gr. 4 + gr. 2 CaO.

Titolo calcolato	...	34,9 % a.t.
Trovato 1907	...	36,0 % a.t.

Anche riguardo alla correzione da farsi a resultato finale siamo di parere che niente debba mutarsi dalle regole 1898, avendo riconosciuto giusto il progressivo aumento della detrazione da farsi dalle materie con 20 % A.T. fino a 50 %.

Perchè se è vero che diminuisce il residuo coll'aumentare della percentualità in A.T. non basta questo a compensare né tanto meno a diminuire la sensibilità d'errore causa l'aumentata concentrazione della soluzione. Per materie a 50 % oltre ad aver già ridotto a metà il campione da assaggiarsi si compensa il piccolo errore del residuo col portare la soluzione a 100,5 anzichè a 100, appunto perchè il residuo si è riscontrato pressochè costantemente gr. 0,5 e perciò non fa bisogno di correzione.

L'unica accettabile modificazione al metodo 1898 e che non ha altro scopo d'un po' di guadagno di tempo é l'attacco con acido cloridrico fatto per soli 10 minuti di digestione anzichè due ore, avendo praticamente riscontrata quasi immediata l'azione dell'acido cloridrico sulle materie tartariche finemente polverizzate e varie prove di confronto non ci hanno dato differenze tanto nell'uno che nell'altro caso.

Ciò premesso riportiamo qui le prescrizioni da seguirsi:

" 6 gr. di feccia finemente macinata e polverizzata, oppure 3 gr. se trattasi di materie superiori a 50 %, si trattano con 9 c.c. d'acido cloridrico, densità 1,1 lasciandoli a digerire per 10 minuti, agitando spesso affinchè tutta la massa possa ben venire in contatto dell'acido cloridrico. Si spruzza tutto con acqua distillata in un palloncino da 100 c.c. Si porta giusto fino al segno e dopo agitato ben bene si filtra pel filtro a pieghe asciutto in un recipiente asciutto.

50 c.c. del filtrato che dovranno controllarsi esattamente corrispondenti alla metà di 100 c.c. del palloncino, si portano in un bicchiere dove si dovranno trovare 18 c.c. di soluzione di potassa al 20 %.

Si fanno bollire per 10—15 minuti fino a che il carbonato di calcio si deposita polverulento. Indi si filtra il tutto per un filtro a succione, si lava bicchiere e precipitato con acqua calda e si porta il filitrato in una cassula di porcellana (comodamente tarata per 15 c.c.).

Si evapora a bagno maria fino a 15 c.c., dopo si tratta con c.c. 3,5 d'acido acetico agitando per 5 minuti. Si aggiungono quindi 100 c.c. d'alcool a 95 %, e si mescola bene la soluzione per altri 5 minuti.

Dopo 10 minuti si può filtrare pel filtro a succione e si seguita a lavare con alcool fino a che il lavaggio non segna più reazione acida.

Filtro e precipitato insieme si portano quindi in un bicchiere da titolazione con circa 200 c.c. d'acqua bollente.

Si titola la soluzione con soda 1/5 normale, adoprando come indicatore la carta di tornasole.

La soda deve essere titolata con cremore chimicamente puro adoprando lo stesso indicatore.

I c.c. di soda occorsi danno direttamente la percentuale in A.T. della materia analizzata in caso siano stati presi 6 gr. in caso di 3 grammi la stessa percentuale si otterrà moltiplicando per 2 il numero dei c.c di soda.

Per compensare poi il volume della parte insolubile della materia greggia non tenuto in conto el riempire fino a segno si farà una detrazione dal resultato finale di 0,7 per le materie con contenuto del 20 % in A.T. e 0,7 più N × 0,02 per la materia con contenuto di 20 + N %.

Per materie a 50 % e più non si farà nessuna correzione, ma invece di portare la prima soluzione a c.c. 100 si porterà a c.c. 100,5.

Discussion.

Dr. O. Tobler.—Tanto la proposta per le modificazioni al metodo Goldemberg, quanto la richiesta d' un metodo ufficiale per la ricerca del piombo nell' acido tartarico e citrico, en proporta de' relatori viene rimandata all' esame dell XI commissione internazionale d' analisi, concordando in ciò anche il Prof. Fresenius.

Professor W. Fresenius sagte:—"Für die Bestimmung des Bleies in Weinsteinsäure hat sich die Methode von Kühn (Arbeiten aus dem kaiserlichen Gesundheitsamt 23, 389, Zeitschrift für analytische Chemie *46*, 62) mit der Modifikation, dass 100 g. Weinsteinsäure benutzt mit 2 g. Natriumnitrat versetzt in 100 g. Wasser gelöst werden und mit 1,6 g. kristallisierten Natriumsulfid gelöst in 100 cc. Wasser und 5 cc. Eisessig gefällt.

Am Schluss titriert man mit 1/100 Normal-Thiosulfatlösung."

H. Nissenson, Dipl. Ing., Direktor, Stolberg, Rhld., sagte:—"Die Bestimmung des Bleies im Weinstein und Zitronensäure: 10 gr. in 3° cm. HNO_3 (1,4 sp. Gew.) durch Kochen gelöst und dann der Elektrolyse unterworfen."

S. Przibytek, St. Petersburg, sagte:—"Die Methoden und Vorschriften für die Bleibestimmung im Wein muss verallgemeint sein auch für die Analyse der künstlichen Mineralwässer, Zucker-, Wein- und Zitronensäure in Nahrungsmittel."

Sous-Section des Lies et Tartres.
Prises d'échantillons.

Par Dr. P. Carles.

Quoique la sous-commission ne se soit encore occupée que de certaines méthodes analytiques, il nous semble qu'elle a le devoir aussi d'étudier l'échantillonnage qui est en analyse une question préjudicielle de premier ordre. Comme, à plusieurs reprises, on nous a consulté à ce sujet, à l'étranger surtout, nous allons écrire ce que nous avons répondu. Cela incitera les intéressés et les compétents à ajouter leurs observations soit antérieurement au Congrès, soit à la séance elle-même.

Les matières tartreuses brutes, les lies et les tartres surtout, représentent toujours une marchandise de composition irrégulière; et cette irrégularité s'accroit d'autant plus en général, que les lots sont plus volumineux. Cela tient à ce qu'ils sont constitués par des mélanges naturels ou provoqués de matières d'origine des plus diverses.

Matières en tas.—Dans les cas les plus courants, les lots sont formés par un tas accumulé au milieu d'un grenier ou d'un hanger. Pour uniformiser tout cela, le tas de forme conique est attaqué à la pelle par deux hommes qui se font face, l'un agissant de la main droite surtout, l'autre de la main gauche et le tout est ainsi roulé successivement d'un bout de grenier ou de hangar à l'autre. A ce terme, les deux hommes agissent de même dans le sens opposé ; puis ils remontent le tout au milieu. Là, ils en refont une pile conique. Ce tas est ensuite ouvert régulièrement, en procédant sur le pourtour en limaçon de façon à le transformer en une vaste nappe ronde. Le diamètre de cette nappe devra être triple au moins de celui de la base du côté primitif.

1[ère] *Prise.*—Cela fait, à l'aide d'une pelle, on prélève ça-et-là sur cette nappe, une série de petites prises dont la réunion représente 1 % environ de la masse totale. On la crible à part et la matière qui refuse de passer est écrasée à la dame. Par ce mot, on entend des masses en bois ou en fer, coniques généralement et à base plane que l'on manie avec un manche à la façon d'un pilon.

On opère sur un sol en pierre, en brique et mieux en ciment.

Quand la matière suffisamment divisée est entièrement passée au crible sans aucun résidu, deux hommes se faisant face comme au début, la poussent par petites pelletées, d'abord sur la droite, puis sur la gauche, la mettant en tas conique, puis en nappe ronde. Enfin avec une petite pelle à main, ils prélèvent deci-delà un nouvel échantillon de la masse criblée, de façon a en réunir environ 1 % et ils le portent au moulin à bras.

Deuxième Prise.—Au sortir de ce moulin, la poudre bien mélangée encore* est divisée en trois ou en un plus grand nombre d'échantillons de 200, 300, 500 gram. selon sa nature et sa destination. On la plie dans deux ou trois papiers forts, de façon à ce qu'elle soit en couches épaisses et serrées à angles bien pleins. Au surplus on retient le paquet avec une ficelle dont on immobilise les bouts avec un cachet de cire.

Troisième Prise.—Il est entendu qu'avant d'être soumise à l'analyse, cette matière doit être le plus souvent moulue derechef et d'autant plus finement qu'elle est plus riche et surtout mieux cristallisée. Certains cristaux de marc ou d'alambic notamment (qu'on mélange parfois aux lies pauvres) exigent pour les essais que toute matière où ils se trouvent soit réduite en poudre impalpable et même, pour plus de sûreté passée au tamis No. 90, mais sans aucun résidu!

Quand il s'agit de lots importants par leur volume ou leur qualité et destinés à n'être titrés qu'à longs intervalles ou après transport de mer, il est prudent d'enfermer les échantillons non plus dans des papiers, mais dans des flacons de verre. De cette façon, ils ne peuvent plus être influencés par l'humidité ou la sécheresse naturelle intervenues entre deux essais pratiqués à des jours différents. D'ailleurs de cette manière, nul n'a plus le pouvoir de les dessécher ou de les saturer d'humidité, selon son intérêt en les tenant auprès du feu ou en les laissant séjourner à la cave. Nous indiquons plus loin dans quelles limites ces influences naturelles ou artificielles peuvent agir. N'oublions pas qu'artificielles est ici synonyme de frauduleuses.

Matières en sacs.—Lorsque les matières tartreuses sont en sacs, il

* Chaque fois qu'une matière tartreuse vient d'être moulue ou tamisée, il y a lieu de la remélanger. On y arrive avec les mains à doigts écartés, une carte, une spatule, un large couteau ou même un autre tamis à mailles plus larges que le premier. C'est absolument nécessaire parce que le moulin et le tamis font une sélection entre les parties d'inégale grosseur, d'inégale dureté, et même d'inégale densité.

y a lieu de voir avant tout, en en vidant entièrement quelques uns, si elles paraissent de composition uniforme ou non. Dans les deux cas, il ne faudrait pas songer à prendre des échantillons par sondages, parce que la sonde évite les gros cristaux, les matières dures et prend de préférence les poussières et les parties tendres. Ceci marque qu'un sondage est généralement défavorable à la proportion des produits cristallisés riche. Aussi est-il préférable de vider sinon tous les sacs, du moins un nombre d'autant plus grand que la matière a plus de valeur. On en fait alors un tas et on procède ensuite comme nous l'avons établi plus haut.

On peut encore chaque cinq ou dix sacs, selon la régularité de la matière, en faire coucher un, l'éventrer à la couture et prendre alors autant que possible au centre même une pelletée de matière qui servira à constituer l'échantillon moyen. On procédera pour cela par pelletage, étendage, trituration à la dame et mouture, ainsi qu'il a été dit.

Toile à tartres.—Quand il s'agit de matières tartreuses à grain à peu près égal, on gagne du temps à les réunir sur une toile où il est aisé de les faire courir dans tous les sens, les unes sur les autres, en relevant les coins et les bords et en agissant, du reste, comme sur le ciment ou le carreau.

Manœuvres frauduleuses sur les échantillons.—D'après des expériences que nous avons détaillées (Dérivés tartriques du vin 3ème edition p. 77) on peut, en desséchant les paquets d'échantillons, augmenter leur degré et l'abaisser au contraire en les tenant à la cave. Mais on aurait tort d'exagérer outre mesure l'importance de ces manœuvres frauduleuses. D'abord parce que l'augmentation, selon la matière, ne va pas au-delà de 1 degré $\frac{1}{2}$ et la diminution au dessus de 1 degré; et ensuite surtout parce que au bout de 36 à 48 heures d'exposition à l'air libre l'équilibre normal s'est rétabli. Le remède est donc aisé à appliquer.

Lies Vertes.—Quand il s'agit de lies vertes, sortant de la presse et contenant encore en moyenne 50 % d'humidité, il est essentiel de prendre des échantillons sur toutes les parties externes, moyennes et centrales. On les malaxe à la main, au pilon ou mieux entre des cylindres allant en sens inverse, ou encore on les hache avec un couteau, et on en prélève finalement deux à trois cents gram. on les chauffe au four ou à l'étuve progressivement en divisant les mottes jusqu'à ce que à 100 ou à 105 degrés le poids reste invariable entre

deux pesées consécutives. Cette haute température est nécessaire pour les lies pectineuses de certains raisins blancs surtout. Il ne reste plus qu'à moudre la matière et à la soumettre à la méthode de dosage convenue.

Quand on a le rendement des lies desséchées, il est aisé par un simple calcul de le reporter sur les lies vertes ou humides; puisqu'on a avant tout pris note du poids de l'échantillon de la matière verte mise en œuvre, soit 200 gram. par exemple.

Dr. OSCAR TOBLER read a Paper on

Ricecra del piombo nell' acido tartarico e citrico.

Sulla determinazione del Tannino nei liquidi concianti mediante l'impiego del refrattometro ad immersione di Zeiss.

P. Falciola e M. Corridi.

Queste ricerche furono eseguite allo scopo di portare un contributo alla determinazione del tannino nei liquidi concianti mediante l' impiego del refrattometro ad immersione di Zeiss. È noto, del resto, come questo apparecchio tenda sempre più ad entrare nell' analisi tecnica.

L' argomento, che presenta un grande interesse per la chimica analitica, fu studiato per la prima volta da C. Zwick; egli, infatti, per il primo, ha proposto l' impiego del refrattometro per l' analisi dei liquidi concianti. Ma, per stabilire se tale metodo di analisi sia veramente suscettibile di applicazioni pratiche, è bene venga assoggettato da diverse parti ad una estesa prova sperimentale in maniera da poter determinare definitivamente gli equivalenti refrattometrici medî delle diverse sostanze tannanti.

Tralascieremo di descrivere il procedimento, che presenta notevoli vantaggi su quello puramente chimico e che costituisce il metodo ufficiale dell' A. I. C. I. C. (Associazione internazionale dei chimici dell' industria del cuoio). Con quest' ultimo, è noto, si determina per evaporazione il residuo totale del campione e, d' altra parte, il residuo della evaporazione, ma dopo opportuna detannizzazione con polvere di pelle; la differenza delle due determinazioni fornisce il tannino contenuto nel campione analizzato.

Col metodo refrattometrico noi abbiamo operato così: scioglievansi in acqua circa 15 gr. di estratto e portavasi ad un litro; si filtravano le soluzioni attraverso a candele porose e si assoggettavano poscia all' osservazione refrattometrica prima e dopo detannizzazione opportuna, eseguita col filtro a campana Procter. Per controllo in altre porzioni del liquido si determinava collateralmente il tannino per via gravimetrica.

Si ottennero i risultati seguenti:

Estratti tannici.	Numero delle osservazioni al refrattometro.	Numeri limiti.	Equivalenti refrattometrici medî.
Mirabolani	5	0·160÷0·175	0·171
Vallonea	9	0·175÷0·193	0·181
Mimosa	5	0·166÷0·173	0·170
Quebracho	5	0·161÷0·171	0·168
Pino toscano	2	0·150÷0·170	0·160
Quercitrone	2	0·176÷0·178	0·178
Castagno	2	0·175÷0·176	0·176
Sommaco	1	0·172	0·172
Giallo Cuba	1	0·160	0·160

L'accordo collo Zwick è quasi perfetto per gli estratti di quebracho: egli trova 0·169 invece di 0·168; vi è invece una differenza molto sensibile per gli estratti di mirabolani, avendo egli trovato 0·189 invece di 0·171.

Le differenze fra i numeri rappresentanti gli equivalenti refrattometrici medî dei varî estratti sono tali che non lasciano intravvedere la possibilità di riuscire, col mezzo del refrattometro, ad identificare la natura dei diversi estratti.

I risultati delle presenti esperienze erano già stati presentati a Roma, alla Commissione Giudicatrice pel premio da conferirsi ai giovani chimici italiani desiderosi di recarsi al VII. Congresso, quando è apparso nel *Collegium* (fascicoli 24 aprile e 1 maggio) un lavoro di I. Sager, fatto nella Deutscher Gerberschule di Freiberg e che giunge a risultati non molto diversi da questi.

The action of Iodine on Phenols, with special reference to a rapid method of estimating Tannic Acid.

By Walter M. Gardner, M.Sc.,
and Herbert H. Hodgson, M.A., B.Sc., Ph.D.

ABSTRACT.

The object of the work described in this paper was to devise a rapid quantitative method for the estimation of tannic and gallic acids.

From the known constitution of gallic acid and also from a consideration of the formulæ ascribed to tannic acid, a quantitative yield of benzoic acid might be expected on reduction. Bottinger (Annalen 258, pp. 252-260), acting with metallic sodium in absolute alcohol, obtained no reduction product, but Guignet (Compt. Rend., 1891, pp. 130-200, J.S.C.I., 1892, p. 261) found that both tannic and gallic acids yield benzoic acid when treated with zinc dust in acid or alkaline solution.

The authors submitted tannic acid to the action of reducing agents under various conditions, and found that little or no reaction takes place in neutral or acid solution, but that tannic acid is very reactive towards alkaline reducing agents. In no case was a quantitative yield of benzoic acid obtained, this being due to the fact that benzoic acid itself is slowly destroyed by alkaline reducing agents.

The reducing agents employed were:—

1. Zinc (with ammonia, ammonium chloride, various acids, and as zinc-copper couple).
2. Sodium (in alcohol and in moist ether).
3. Magnesium (with hydrochloric acid, ammonium chloride, and potassium carbonate).
4. Aluminium (with sodium hydrate).
5. Sodium Hydrosulphite.
6. Hydriodic Acid.

In a number of cases the production of benzoic acid was demonstrated, but in no case was the result of quantitative importance, and although the conditions of concentration, time of reaction, and

nature of atmosphere were widely varied the result was invariably unsatisfactory. One general observation was, however, of interest, viz., the tendency of tannic and gallic acids to form reduction products under alkaline conditions, and this is further borne out by experiments made with alkaline iodides which have given much more satisfactory results as shown in the next section of the paper.

The action of Iodine on Phenols, including a process for the estimation of Tannic Acid.

Messinger and Vortmann have shown (Ber., 1890, p. 2753, J.S.C.I., 1890, p. 1070) that phenol absorbs iodine in the presence of alkaline hydrates, but they were unable to obtain satisfactory quantitative results.

F. Musset (Chem. News 51, p. 42) has described a method of titrating tannin with iodine, but by his method the absorption required twelve hours, the excess of iodine being subsequently estimated by titration with thiosulphate. The "non-tannins" were estimated in a second experiment after precipitating the tannic acid by means of gelatine.

A. Moullade (Jour. Pharm. Ch. XXII., p. 153) titrated tannic acid with iodine in presence of sodium bicarbonate, using carbon disulphide as indicator. He states that it is necessary to take the mean of several titrations in order to ensure accuracy, and he estimates the non-tannins in the usual manner. All the above-mentioned methods are thus defective, Musset's process requiring at least twelve hours, and that of Moullade being deficient in accuracy.

The modified method which the authors propose can (apart from the gelatine precipitation or hide powder absorption) be carried out completely in a few minutes, and shows a definite end-point. Concordant results are obtained not only with tannic acid, but with many other phenolic substances. Within the range of phenols dealt with, a certain number were found to require one molecule of iodine for each hydroxyl group, whereas in other cases, though the results were strictly quantitative, they were empirical in the sense that no ratio could be traced between the iodine absorbed and the number of hydroxyl groups in the molecule.

The general method is as follows:—A standard aqueous solution of the substance is prepared (in the case of tannic acid, 1 gr. per litre), and to a known volume of this solution (20 c.c.) diluted to 200 c.c., with water, standard N/10, iodine solution is added in excess (20 c.c.).

A few drops of starch solution are then added, and afterwards aqueous sodium hydrate is run in drop by drop until the colour due to the iodine disappears. By this means excess of alkali, which has an injurious effect on the accuracy of the process, is avoided. Dilute hydrochloric or sulphuric acid (1 in 4) is added in sufficient excess (50 c.c.) to separate the unabsorbed iodine, the amount of which is estimated by standard N/10 thiosulphate.

In the case of the following phenols the amount of iodine absorbed is exactly one molecule for each hydroxyl group present—phenol, catechol, hydroquinine, pyrogallic acid and gallic acid.

No theory is put forward with regard to the course of the reaction.

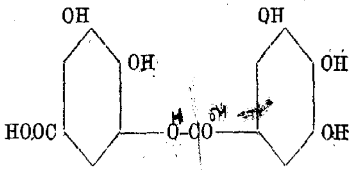
The presence of such groups as NO_2,NH_2, and O·Me., as well as the position of the hydroxyls in the benzene nucleus was found to have a determining effect on the course of the reaction. For example, the weak phenolic properties of the hydroxyls in para-oxybenzoic acid result in there being no absorption of iodine. The presence of nitro or methoxyl groups also protects the hydroxyl group from attack, while in para-amidophenol a definite quantitative absorption was observed, which, however, did not correspond to one hydroxyl. The alcoholic hydroxyl group, *e.g.*, in benzyl alcohol, is also unaffected under the conditions of the process.

Phloroglucinol, which possesses both phenolic and quinolic properties, gave an absorption equivalent to two hydroxyls, whereas the isomeric pyrogallic acid behaved normally, the three hydroxyls absorbing three molecules of iodine. A similar normal result is obtained with gallic acid.

In the case of gallotannic acid a large number of experiments were made under varying conditions of concentration, amount of excess of iodine, etc., and perfectly concordant results were always obtained. The process is, therefore, available for the quantitative estimation of gallotannic acid, and is applicable to the commercial tannins. Two estimations are, of course, necessary. Firstly, that of the total iodine absorbed by the standard solution of the tannin, and secondly, that of the iodine absorbed after removing the tannic acid from the solution by precipitation with gelatine or absorption by hide powder; the difference in the two estimations giving the iodine absorbed by the tannic acid itself.

In the case of pure tannic acid the absorption was found to correspond to eleven atoms of iodine for each molecule of tannic

acid, on the supposition that tannic acid may be regarded as digallic acid.



The above formula shows the presence of five hydroxyls requiring ten atoms of iodine, and it may be assumed that the chain connecting the benzene nuclei is responsible for the absorption of the additional atom of iodine.

The very rapid absorption of iodine in presence of alkali, which occurs in the method for the estimation of phenols suggested in this paper, is very probably due to the formation of hypoiodates which Wigs has shown in his work on Hubl's solution (Zeit. Angew. Chem., 1898, 291-297; Ber., 1898, 750-752) re-acts very readily.

Comparison between the results obtained with the iodine process described, and those given by the standard Löwenthal method, when applied to a number of the ordinary commercial tannin-containing materials, showed a close agreement in all cases.

Tannic Acid.

For the experiments with this substance, a sample of pure tannic acid (Kahlbaum) was used. 0·02 grms. required as the mean of a large number of closely agreeing titrations 7·15 c.c. N/10 iodine. After precipitating the tannic acid by gelatine an absorption of 0·3 c.c. N/10 I was given by 20 c.c. of the residual solution. The corrected amount of iodine absorbed was therefore = 0·08698 grms. 0·02 grms. tannic acid requires for five OH groups 0·0788 grms. iodine ($5I_2$) and for six OH groups 0·0946 grms. ($6I_2$). On the supposition that eleven atoms are absorbed by one molecule gallotannic acid, the amount of iodine required by 0·02 grms. gallotannic acid = 0·0876 grms., which figure is in practical agreement with the experiments.

In order to test the reliability of the method a large number of analytical results were obtained with widely differing quantities of the substances used.

Concentration of Tannic Acid Solution.

Strength of Tannic Acid used = 1 grm. per litre.

40 c.c.	Tannic	Acid	solution	absorb	14·25 c.c.	N/10	Iodine
35 c.c.	,,	,,	,,	,,	12·45 c.c.	,,	,,
30 c.c.	,,	,,	,,	,,	10·70 c.c.	,,	,,
25 c.c.	,,	,,	,,	,,	8·90 c.c.	,,	,,
20 c.c.	,,	,,	,,	,,	7·15 c.c.	,,	,,
15 c.c.	,,	,,	,,	,,	5·35 c.c.	,,	,,
10 c.c.	,,	,,	,,	,,	3·55 c.c.	,,	,,
5 c.c.	,,	,,	,,	,,	1·80 c.c.	,,	,,

In each case the solution was diluted to 200 c.c. with water.

Concentration of Iodine Solution.

The experiments were repeated, using N/50 I and N/50 $Na_2S_2O_3$. Factor for thiosulphate $= \frac{10}{9.75}$.

20 c.c. tannic acid require 34·00 N/50 iodine expressed as $Na_2S_2O_3$. (Calculated = 34·87 c.c.)

15 c.c. tannic acid require 25·65 N/50 iodine expressed as $Na_2S_2O_3$. (Calculated = 26·30 c.c.)

10 c.c tannic acid require 17·1 N/50 iodine expressed as $Na_2S_2O_3$. (Calculated = 17·53 c.c)

5 c.c. tannic acid require 8·55 N/50 iodine expressed as $Na_2S_2O_3$ (Calculated = 8·76 c.c.

From the range taken it will be seen that the iodine absorption is perfectly regular and trustworthy.

Comparison of the Iodine with the Löwenthal Method.

The results are expressed in percentages of tannic acid, the Kahlbaum pure tannic acid being taken as standard.

Tannins.	Extract.	Löwenthal. percentage.	Iodine. percentage.
Gall-nuts ...	No. 1 ...	66·47 ...	65·3
	No. 2 ...	64·02 ...	65·62
	No. 3 ...	60·40 ...	60·28
	No. 4 ...	63·61 ...	63·14
	No. 5 ...	62·59 ...	62·09

Tannins.		Extract.		Löwenthal. percentage.		Iodine. percentage.
Sumac ...	...	No. 1	...	22·84	...	21·26
		No. 2	...	22·51	...	20·14
		No. 3	...	16·57	...	16·08
		No. 4	...	17·20	...	16·78
Myrabolams	...	No. 1	...	26·06	...	27·27
		No. 2	...	27·52	...	27·44
		No. 3	...	29·33	...	29·74
		No. 4	...	31·24	...	31·12
Valonia	...	...	...	28·11	...	28·67
Dividivi	...	...	...	33·00	...	31·47
Quebracho	...	...	...	13·63	...	13·28

The advantages of the iodine process are that it is more quickly carried out than the Löwenthal method, and in the titration the end-point is absolutely sharp; whereas in the older method a considerable personal equation is involved in the final reading, and the results obtained are influenced by the speed with which the permanganate is added and by other variations in the process.

General Conclusions.

The absorption of iodine in alkaline solution appears in certain cases to take place in definite molecular proportions, but in other cases is empirical though quantitative amount. The absorption takes place most readily in the case of bodies with pronounced phenolic properties, and is in some cases entirely prevented by the presence of other groups in the benzene nucleus. The method described in the paper is, however, available for the quantitative determination of tannic acid and other substances, and involves no complicated or lengthy process, nor the observation of an indefinite end-point. It appears, therefore, of practical importance.

TECHNICAL RESEARCH LABORATORY,

BRADFORD TECHNICAL COLLEGE.

Sur le Dosage du Phosphore dans les Fers, Fontes et Aciers.

Par G. Chesneau,
Professeur d'Analyse Minérale à l'Ecole des Mines de Paris.

Résumé.

Ayant constaté récemment des écarts notables dans les teneurs de phosphore obtenues pour un même acier par les méthodes d'analyse considérées comme les plus sûres, j'ai été amené à faire une étude approfondie sur la précipitation du phosphore sous forme de phosphomolybdate d'ammoniaque en vue du dosage de cet élément dans les fers, fontes et aciers. Cette étude m'a conduit aux conclusions suivantes.*

1. La précipitation complète du phosphore en présence du fer n'est réalisée qu'en observant un certain rapport entre les concentrations respectives du fer, de l'acide molybdique et du nitrate d'ammoniaque, en présence desquels se fait la précipitation.

2. Le poids du précipité peut subir une diminution par l'emploi de liquides de lavage acides ou nitratés, et il est préférable de le laver à l'eau pure. Il peut en revanche se produire des surcharges considérables par précipitation de tétramolybdate d'ammoniaque, dont la formation est favorisée par l'élévation de température.

3. Le précipité de phosphomolybdate ne doit pas être considéré comme un composé défini véritable, mais plutôt comme un mélange d'un composé défini avec de l'oxyde molybdique (ou du tétramolybdate d'ammoniaque) qui, suivant les concentrations respectives des corps existant dans l'eau mère fait osciller la proportion de phosphore entre 1 et 2 pour cent environ. Ces variations de composition sont en rapport avec les formes cristallines du précipité observé sous fort grossissement (plus de 200 diamètres), et à cet égard l'emploi du microscope peut rendre les plus grands services pour apprécier *à priori* la pureté relative du précipité : en liqueur nitrique sans sels ammoniacaux, on obtient des cristaux jaune vif formés de cubes, octaèdres et surtout dodécaèdres rhomboïdaux, contenant de 1,7 à 2,2 % de phosphore ; en liqueur de nitrate d'ammoniaque légèrement

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* Voir pour le détail des expériences le mémoire que j'ai publié dans la "Revue de Métallurgie." (Vol. V., No. 5, page 235 ; 1908.)

acide, le précipité est formé de beaux cristallites jaune pâle en forme d'étoiles à six branches ou de croix (1,60 % de phosphore); enfin, avec un très grand excès de nitrate d'ammoniaque par rapport au phosphore, les cristallites sont empâtés et plus pâles, et mélangés de prismes incolores de tétramolybdate d'ammoniaque (teneur en phosphore descendant jusqu'à 1 %).

4. Par précipitation simple, il est impossible d'obtenir un phosphomolybdate à teneur constante en phosphore; au contraire en redissolvant le précipité par l'ammoniaque et le reprécipitant par l'acide nitrique, on peut obtenir, moyennant certaines précautions, un phosphomolybdate de composition sensiblement constante (1,60 % de phosphore).

Le mode opératoire auquel je me suis arrêté à la suite de mes recherches est le suivant, modifiant et complétant la méthode de A. Carnot :

Méthode de dosage proposée.

1. Opérer sur des prises d'essai de 1 gr. pour les fers et aciers et les fontes pures, sur 0 gr. 5 à 0 gr. 2 pour les fontes phosphoreuses, de façon à n'avoir jamais plus de 6 mmg. de phosphore à précipiter (au-dessus de ce poids, le précipité est trop abondant pour pouvoir être lavé sur très petit filtre).

2. Attaquer à froid par 20 cmc. de NO^3H ($d=1,20$), compléter l'attaque en chauffant doucement, ajouter 2 cmc. exactement mesurés de SO^4H^2 concentré, évaporer à sec et insolubiliser la silice à 125° C. Redissoudre par 50 cmc. d'eau chaude, filtrer; ajouter au filtrat 1 gr. d'acide chromique cristallisé pur, et concentrer l'ébullition jusqu'à environ 20 cmc.

3. Ajouter au liquide 5 gr. de nitrate d'ammoniaque en cristaux, puis, après dissolution de ce sel, 50 cmc. de réactif molybdique [contenant par litre : 50 gr. de molybdate d'ammoniaque, 50 cmc. d'ammoniaque concentrée et 500 cmc. de NO^3H ($d=1,20$), ce réactif étant préparé à froid peu de temps avant usage]. Chauffer pendant $1\frac{1}{2}$ heures entre 65° et 70° C., en agitant tous les quarts d'heure, puis laisser refroidir.

4. Laver le précipité de phosphomolybdate avec de l'eau à 5 pour cent de réactif molybdique, le redissoudre dans 50 cmc. d'un mélange chaud de 1 vol. d'ammoniaque concentrée et 3 vol. d'eau. Saturer l'ammoniaque jusqu'à réaction acide par de l'acide nitrique concentré versé goutte à goutte, en refroidissant le mélange sous un

jet d'eau. Le précipité s'étant reformé en majeure partie, ajouter au bout de ¼ d'heure, 15 cmc. de réactif molybdique, et chauffer 2 heures dans une étuve réglée à 40° C., pour compléter la précipitation.

Laver le précipité à l'eau pure, trois fois par décantation et six fois sur petit filtre de 8 cm. de diamètre (filtre Schleicher dur No. 602). Dissoudre le précipité par un peu d'ammoniaque diluée chaude, recueillir le liquide dans une capsule de platine tarée, évaporer doucement à sec, puis chauffer progressivement jusqu'à 400° à 450°, sur la toile d'un fourneau à gaz qu'on fait rougir à la fin, sans que le fond de la capsule atteigne lui-même le rouge naissant. Le pyromolybdate bleu ainsi obtenu contient 1,69 pour cent de phosphore.

Comme contrôle on peut peser d'abord sous forme de phosphomolybdate jaune, en opérant sur filtre taré, desséchant 1½ heures à l'étuve à 105° C., laissant refroidir dans un exsiccateur à SO^4H^2 concentré *frais*, et pesant dans un flacon bouché à l'émeri: le phosphomolybdate jaune obtenu ainsi contient 1,60 pour cent de phosphore.

Au cours de la filtration du phosphomolybdate de 2e précipitation, on ne devra pas omettre de vérifier au microscope la forme des cristaux, ce qui permettra de rectifier au besoin le coefficient à employer, si leur aspect dénote la présence de tétramolybdate d'ammoniaque, ce qui pourrait arriver, surtout pour des précipités de faible poids, au cas où l'on aurait négligé d'observer strictement toutes les précautions précédentes.

Capitaine Nicolardot confirme les résultats signalés par M. Chesneau. Les dosages du phosphore qui étaient exécutés au laboratoire de la section technique de l'artillerie par double précipitation à l'état de phospho-molybdate puis sous forme de phosphate ammoniacomagnésien, avaient été parfois contestés; depuis que la précipitation phosphore est exécutée, suivant les indications publiées par M. Chesneau, aucune contestation ne s'est encore produite.

Analyse des Ferrosiliciums contenant moins de 30 % de Silicium.

Par Paul Nicolardot.

Les ferrosiliciums contenant plus de 20 % de silicium ou, pour une teneur moindre en silicium, quand ils renferment une notable proportion de manganèse, ne s'attaquent plus par l'eau régale. J'ai reconnu que leur attaque par les carbonates alcalins en fusion est d'autant plus rapide et plus complète que la quantité de carbonates mise en œuvre est la plus faible possible ; mais j'ai cherché à éviter la porphyrisation de l'échantillon, l'emploi de creusets de platine et surtout celui de réactifs fixes par l'emploi d'un autre agent d'attaque.

Le chlorure de soufre S_2Cl_2 est volatil, et, à part le soufre, n'introduit dans le dosage aucun des corps que l'analyse conduit à rechercher dans les ferrosiliciums.

Trompe.

Mode opératoire.—Dans un ballon à fond rond de 250 cm.c. bien sec, on introduit 0 gr. 5 de ferrosilicium pulvérisé. Le ballon est fermé par un bouchon en caoutchouc traversé par un tube de verre muni d'un robinet dont la partie inférieure est terminée en sifflet. La partie extérieure du tube est formée de deux cylindres de diamètre différent. La partie étroite est graduée par demi-centimètres cubes ; sur la partie large se place un bouchon traversé par un tube relié à une trompe.

On fait le vide jusqu'à 20 cm. de mercure et on ferme le robinet. On verse 2 cm.c. de S_2Cl_2, qu'on introduit peu à peu, et on chauffe. Dès que l'attaque commence, on cesse de chauffer. Le chlorure de soufre qui n'a pas réagi coule vers le bas. Il suffit de chauffer pour rendre l'attaque complète. Après refroidissement, on introduit peu à peu de l'eau ammoniacale, on retourne plusieurs fois le ballon avec le robinet fermé de manière à décomposer tout le chlorure de silicium. Le dosage des divers éléments est exécuté ensuite suivant les méthodes ordinaires.

Analyse du Wolfram et de la Hübnerite.— Séparation de la Silice et de l'Acide tungstique.

Par Paul Nicolardot.

Les tungstates naturels (wolfram et hübnerite), si difficiles à attaquer, même après porphyrisation par les réactifs ordinaires, réagissent avec énergie sur les alcalis en fusion. En quelques secondes les fragments obtenus après un broyage sommaire sont attaqués par la potasse ou la soude fondue. Il suffit ensuite de reprendre par l'eau et de séparer les divers éléments par les méthodes ordinaires.

Seule la séparation de l'acide tungstique et de la silice présente quelques difficultés. Le meilleur procédé connu consiste à traiter le mélange par un courant d'acide chlorhydrique gazeux à 600° au moins. J'ai observé que, dans certaines conditions, la silice pouvait être entraînée en partie.

L'emploi des vapeurs de chloroforme, mélangées d'air incomplètement desséché, permet de séparer, au-dessous de 500°, sans dépôt de charbon, tout l'anhydride tungstique de la silice.

Mode opératoire.—Fondre 2 gr. de minerai pulvérisé avec deux fois son poids de soude caustique dans un creuset de *platine* chauffé au moyen d'une lampe à alcool. Reprendre par l'eau et oxyder par le brôme après filtration. Neutraliser par ClH et filtrer pour recueiller (Al_2O_3, Fe_2O_3, SiO_2. . .). Acidifier légèrement pour précipiter le soufre. Refondre le précipité de sulfate de baryum. Traiter ensuite par H_2S pour As, Bi, Cu, Sn. Concentrer après filtration en acidifiant fortement par AzO_3H ; filtrer le dépôt d'acide tungstique et de silice ; laver, sécher et calciner. Le poids est la somme de ceux de l'anhydride tungstique et de la silice. On entraîne ensuite l'anhydride tungstique seul par le chloroforme. Dans la liqueur on dose le phosphore et on analyse la gangue qui contient presque toute la cassiterite avec le fer et le manganèse.

Analyse des alliages d'Antimoine.

Communication de MM. Nicolardot et Krell.

Dans la méthode classique indiquée par Wöhler, les alliages d'antimoine sont attaqués par l'acide nitrique étendu (D = 1,2) additionné d'acide tartrique. L'attaque est complète parce que tout le nitrate de plomb formé se dissout dans l'acide nitrique de cette densité et parce que la présence de l'acide tartrique empêche l'antimoine de précipiter. Le plomb est éliminé, presque en totalité, à l'état de sulfate de plomb, et la liqueur acide est soumise à l'action de l'hydrogène sulfuré qui précipite avec l'antimoine, le plomb, le cuivre, l'étain, l'arsenic, etc. Les sulfures filtrés sont épuisés par du sulfure de sodium dilué et froid. L'antimoine se dissout à l'état de sulfosel avec l'étain, l'arsenic et des traces de cuivre. Avec un acide on neutralise la solution des sulfosels; et les sulfures précipités sont recueillis sur filtre taré, puis lavés successivement à l'eau, à l'alcool, à l'éther et au sulfure de carbone. Après pesée du filtre une partie du précipité est prélevée, pesée et transformée en sulfure noir par chauffage dans l'acide carbonique.

Ces longues manipulations sont fastidieuses ; elles ne présentent même pas l'avantage d'éviter toute cause d'erreur (entraînement de l'antimoine par le sulfate de plomb, dissolution du sulfure d'antimoine dans la neutralisation des sulfosels). Aussi de nombreux procédés ont-ils été proposés pour remplacer la méthode de Wöhler. Mais, à cause de leur peu d'exactitude, ils n'ont pas remplacé l'emploi des sulfosels pour toute analyse rigoureuse.

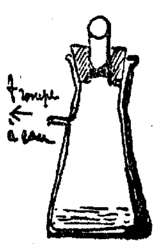
Dans le cas des plombs antimonieux utilisés pour la fabrication des noyaux de balles et de certains caractères d'imprimerie, on peut se servir, assez utilement, des déterminations de Matthiessen* et de Riche.† De la densité de l'alliage, il est possible de déduire sa teneur en antimoine.

* Pogg. Ann., t. cx., p. 28, 1860.
† C. R., t. lv., p. 143 1862.

Nous avons d'abord cherché à éliminer l'emploi de réactifs fixes et nous avons cherché à transformer les alliages en sulfures par l'emploi du soufre fondu ou du sulfure d'ammonium additionné de soufre ou encore par les vapeurs de soufre ou de sulfure de carbone. Ces procédés ne permettent pas d'obtenir facilement les sulfures. Nous avons alors pensé à généraliser la méthode de décomposition des nitrates proposée par Sainte-Claire Deville, et nous avons pu séparer l'antimoine des métaux communs de la même manière que l'on sépare l'acide métastannique.

Le nitrate de plomb desséché et maintenu à 200° pendant un certain temps se redissout encore, même dans l'eau pure, alors que les divers oxydes d'antimoine formés sous l'action de l'acide nitrique restent insolubles, et cela même dans l'acide nitrique. Les autres métaux communs, dont les azotates sont plus ou moins décomposés, se redissolvent dans l'acide nitrique étendu. Seuls les oxydes d'étain et d'antimoine restent insolubles dès que le mélange des nitrates a été chauffé au-dessus de 125°. Pour l'acide métastannique il suffit, comme on le sait, de la température du bain-marie.

Les oxydes d'antimoine obtenus ne peuvent pas être amenés à poids constant, ni sur filtre taré ni par calcination. Il est préférable de les réduire par l'hydrogène, et, pour y arriver plus facilement, sans avoir à détacher le précipité du filtre, nous avons imaginé le dispositif suivant.



La liqueur légèrement nitrique provenant de l'insolubilisation des nitrates à 125°-150° est filtrée dans un petit cylindre en porcelaine poreuse. On essore à la trompe. Le cylindre est pesé vide, après dessiccation à 150°, puis après réduction. L'antimoine et l'étain sont ensuite séparés par les procédés connus et l'étain est dosé seul à l'état de bioxyde qui est fixe à haute température. L'antimoine est évalué par différence.

Cette méthode s'applique très bien aux alliages antifriction. Il suffit de doser le cuivre au pré ́able par électrolyse, la présence des oxydes d'antimoine et d'étain ne gênant pas le dépôt de cuivre. Ce procédé est d'ailleurs le seul qui permette de séparer tout le cuivre entraîné par les oxydes inso!ubles.

Voici pour quelques plombs antimonieux les résultats obtenus par la détermination de la densité et les méthodes aux sulfosels et

aux nitrates. Les deux premières méthodes fournissent des teneurs pour l'antimoine trop faibles en général.

Densité à 15°.	Teneur en antimoine			Plomb %.
	par la densité.	méthode des sulfosels.	par les nitrates.	
11·05	4·1	4·34	4·41	95·15
10·57	10·8	11·32	11·38	88·28
10·41	13·1	12·86	12·92	86·86
8·99	37·2	37·12	37·93	62·05

Question proposée pour la Discussion.

Par M. Paul Nicolardot.

Colombium ou Niobium? Glucinium ou Béryllium?—Il y a intérêt à simplifier les dénominations des éléments. Le même métal est appelé en Amérique *colombium* et en Europe *niobium*. Les pays de langue allemande désignent sous le nom de *béryllium* l'élément appelé par les pays latins et ceux de langue anglaise, *glucinium*. Il conviendrait d'abandonner les noms de *niobium* et de *béryllium* et d'adopter uniquement ceux de *colombium Cb* et *glucinium G*.

Étude des gaz dégagés par l'action des sels cuivriques sur les aciers (dosages du CO_2 et du CO).

Par E. Goutal,

Chef des travaux chimiques à l'École des Mines de Paris.

L'Étude des gaz dégagés par l'action du chlorure double de cuivre et de potassium sur les produits de la métallurgie du fer, nous ayant paru susceptible d'apporter une contribution nouvelle à la connaissance des gaz occlus ou dissous dans les aciers, nous avons établi, dans ce but, le dispositif suivant :

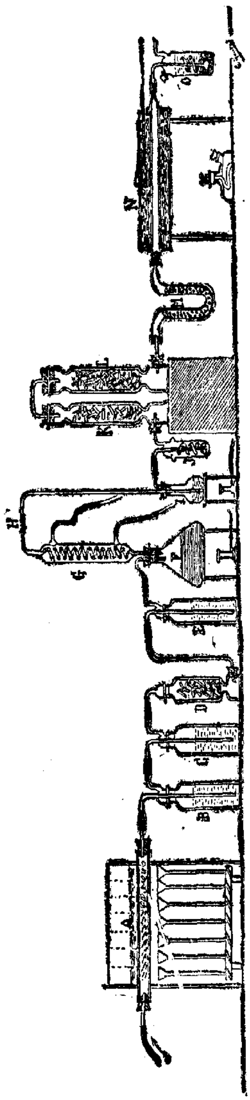
I. Un courant d'azote, provenant de la distillation de l'air liquide, est complètement débarrassé d'oxygène et de produits carbonés par passage : 1° dans un tube de porcelaine A garni d'oxyde et de tournure de cuivre, et chauffé au rouge ; 2° dans deux flacons laveurs B et C, contenant une solution concentrée d'hydrosulfite de sodium ; 3° dans une éprouvette à pied D, remplie de fragments de potasse caustique ; 4° dans un flacon témoin E à eau de baryte.

Ce courant d'azote purifié est conduit dans la partie supérieure d'un flacon conique de 750 c.c. de capacité F, muni d'un serpentin réfrigéré G et placé au-dessus d'un brûleur à couronne. 500 c.c. d'une solution de chlorure double à 40 pour cent sont contenus dans ce flacon avec 4 à 5 gouttes d'acide chlorhydrique.

Le courant d'azote peut ensuite parcourir un système formé : d'un flacon absorbeur I à eau de baryte pour recueillir CO_2, et susceptible d'être chauffé à la fin de l'opération ; d'un absorbeur J à acide sulfurique saturé de vapeurs de brôme ; de deux éprouvettes à pied K et L à potasse caustique ; d'un tube desséchant M à ponce sulfurique ; d'un tube droit à coton de verre et anhydride iodique chauffé dans un bain-marie N, à 75° et destiné à oxyder l'oxyde de carbone, avec mise en liberté d'iode ($I_2O_5 + 5\,CO = 2\,I + 5\,CO_2$) que l'on recueille dans un absorbeur de forme spéciale O, contenant 15 c.c. de chloroforme pur sous une couche d'eau.

Modus Operandi.—Le courant d'azote purifié passe lentement dans le flacon à chlorure double de cuivre et de potassium, dont

le contenu est porté à l'ébullition pendant une demi-heure pour expulser les gaz carbonés qu'il peut contenir.



On réunit ensuite la fiole d'attaque à l'ensemble absorbant qui la suit, et on laisse la solution cuivrique se refroidir tout en maintenant un lent courant d'azote dans tout l'appareil pendant deux heures. L'eau de baryte ne doit pas se troubler et le chloroforme ne doit pas se colorer quoique le bain-marie soit maintenu à 75–80°.

Après ce contrôle, on introduit dans la solution de chlorure de cuivre et de potassium dont la température ne doit pas dépasser 40°, l'échantillon d'acier en limaille ou en fins copeaux, que l'on veut étudier (10 gr.).

L'attaque est conduite à température très modérée, en agitant souvent, jusqu'à redissolution complète du cuivre déposé (deux heures environ). La solution de chlorure double est alors progressivement chauffée jusqu'à l'ébullition que l'on maintient une demi-heure en continuant un lent courant d'azote.

L'anhydride carbonique se trouve alors absorbé par l'eau de baryte dans laquelle il a formé un précipite de carbonate que l'on transforme en sulfate avec les précautions habituelles. L'oxyde de carbone a réduit une partie de l'anhydride iodique, donnant de l'iode libre, dont les vapeurs recueillies dans le chloroforme lui communiquent une teinte plus ou moins rose.

La pesée du sulfate de baryum obtenu et le titrage par l'hyposulfite de l'iode libéré permettent la détermination de l'anhydride carbonique et de l'oxyde de carbone ; sachant que 1 mg. de SO_4Ba correspond à 0 mg. 1889 de CO_2, soit 0·001889 pour cent parties en poids du métal mis en œuvre ; et que 1 c.c. d'hyposulfite à 0 g. 886 de sel par litre correspond à 0 c.c.2 soit 0·0025 pour cent en poids de l'acier soumis à l'essai ; la prise ayant été de 10 gr., comme il est indiqué plus haut.

Le tableau suivant donne quelques exemples des résultats analytiques obtenus :

	Carbone total.	Silicium.	Soufre.	Phosphore.	Manganèse.	CO_2		CO	
						en poids.	en volume.	en poids.	en volume.
Acier doux .	0·160	0·046	0·054	0·015	0·70	0·0250	1 vol.	0·0063	$\frac{1}{3}$
Acier mi-dur .	0·275	0·3400	0·030	0·060	0·75	0·0210	$\frac{4}{5}$ „	0·0120	$\frac{3}{4}$
Acier dur .	0·596	0·0600	0·072	0·033	0·80	0·0678	$2\frac{1}{2}$ „	0·0137	$\frac{4}{5}$
Acier au nickel (Ni = 2·04) .	0·340	0·2570	0·018	0·028	0·56	0·0530	2 „	0·0060	$\frac{1}{3}$
Acier au chrôme (Cr = 5·10) .	0·365	0·1750	0·014	0·031	traces	0·0510	2 „	0·0115	$\frac{3}{4}$
Fonte Martin basique .	4·110	1·1250	0·060	0·040	1·45	0·1890	7 „	0·0132	$\frac{4}{5}$

II. L'appareil précédent peut être modifié dans le but de déterminer directement la quantité totale de carbone dégagé pendant l'attaque au chlorure cuivrique ; d'une part, sous forme de CO_2 ; d'autre part, à l'état de CO, et de composés carbonés divers non encore définis.

Il suffit pour cela de placer après le flacon absorbeur à baryte I un tube de verre de 40 cent. de long, contenant un fil de platine roulé en double spirale sur une longueur de 30 cent., autour d'une baguette creuse en porcelaine maintenue dans l'axe. Ce fil de platine porté au rouge par un courant électrique (3 ampères) permet la combustion des produits carbonés gazeux, grâce à l'introduction d'oxygène pur par un ajutage latéral, pendant toute l'opération.* Le CO_2 ainsi formé est absorbé par de l'eau de baryte et dosé pondéralement, comme ci-dessus. 1 mg. de SO_4Ba correspond à 0 mg. 0514 de C.

Le résidu de carbone recueilli et lavé peut d'ailleurs être brûlé dans

* Disposition analogue à celle adoptée par Breteau et Leroux pour l'analyse organique : Comptes Rendus, 16 sept. 1907.

le même tube ou dans un tube analogue par l'action combinée de l'oxygène pur et du platine porté au rouge ; et l'on obtient ainsi, d'une façon très précise, le dosage du carbone total dans les produits sidérurgiques.

L'application à un même acier des deux méthodes ci-dessus permet la détermination : 1° du carbone résiduel, 2° du carbone dégagé sous forme de CO_2 ; 3° du carbone dégagé sous forme de CO ; 4° enfin de celui dégagé sous forme de composés gazeux non encore définis. Le tableau suivant en donne trois exemples :

	Acier mi-dur.	Acier dur.	Acier extra-dur.
Carbone résiduel	0·2750 %	0·5960 %	1·3340 %
Carbone dégagé sous forme de CO_2	0·0057 %	0·0185 %	0·0216 %
" " " de CO	0·0051 %	0·0059 %	0·0061 %
" " non définie	0·0009 %	0·0171 %	0·0158 %
Carbone total	0·2867 %	0·6375 %	1·3775 %

Ce tableau montre que, pour les aciers courants, la perte en carbone provenant du dégagement de composés gazeux, pendant l'attaque par le chlorure double de cuivre et de potassium presque neutre, dans un courant d'azote, est comprise entre 0·01 et 0·05 pour cent si l'on porte finalement à l'ébullition la liqueur cuivrique contenant le résidu de carbone insoluble.

Ce résultat est voisin de celui trouvé par Moore et Bain opérant à 60° avec une solution de chlorure de cuivre et de potassium contenant 7·5 % d'acide chlorhydrique.*

Si le sel cuivrique est employé presque neutre et vers 40° seulement, et si comme nous l'avons déjà indiqué M. A. Carnot et moi† on prend soin de ne pas sécher à l'étuve avant sa combustion dans l'oxygène le résidu carboné, la perte est moins importante ; en effet, l'anhydride carbonique reste alors entièrement fixé sur le résidu insoluble et l'on ne perd que la portion de carbone correspondant à l'oxyde de carbone et aux produits carbonés non définis qui restent en dissolution dans le chlorure cuivreux ou s'éliminent sous forme gazeuse en faible proportion, pendant l'attaque du métal. Dans les exemples ci-dessus la perte se trouve alors comprise entre 0·006 et 0·026 %.

La perte constatée par l'attaque des fontes est beaucoup plus

* Journ. Soc. Chem. Ind. xxvii. (1908), p. 845.

† Comptes Rendus Acad. des Sciences (12 juillet, 1897).

élevée. Dans le cas d'une fonte blanche de Suède non manganésée, nous avons observé une perte de 0·046 de carbone sous forme d'oxyde de carbone et de composés non définis, tandis que la quantité d'anhydride carbonique formée, et partiellement dégagée pendant l'attaque correspondait à 0·121 % de C. Il est à remarquer que dans le cas des fontes, la fixation de l'anhydride carbonique sur le carbone résiduel n'est pas complète.

Dans tous les cas la détermination du carbone faite sur le résidu obtenu par l'attaque à l'acide du chlorure double de cuivre et de potassium des aciers ou des fontes, ne correspond jamais au *carbone total* de l'échantillon. Pour obtenir ce *carbone total* il est nécessaire d'opérer l'attaque dans une fiole bouchée, parcourue par un courant d'air privé de gaz carbonés, et d'opérer la combustion des gaz carbonés qui se dégagent en disposant par exemple un tube de verre contenant un fil de platine roulé en spirale et porté au rouge par un courant électrique, immédiatement après la fiole où s'opère la dissolution du métal et l'ébullition finale de la solution cuivrique. Le carbone ainsi déterminé sera joint au carbone résiduel dosé d'autre part.

III. La détermination directe de l'oxyde de carbone dégagé pendant l'attaque des aciers, par le chlorure double de cuivre et de potassium, peut encore être obtenue de la façon suivante :

A la suite de la fiole contenant le sel cuivrique, on dispose une série de tubes de Winkler garnis chacun d'une solution à 1 pour cent de sang de cobaye défibriné. Chaque tube absorbeur contenant 25 c.c. de cette solution est susceptible d'absorber une quantité d'oxyde de carbone représentant en poids 0·002 % pour une prise d'essai de 10 grammes. Le courant d'azote doit être alors très lent. Après l'opération, on traite par le sulfure d'ammonium l'hémoglobine des différents tubes absorbeurs, et on l'examine au spectroscope pour déterminer le nombre de tubes présentant le spectre d' absorption de l'hémoglobine oxycarbonique. Ce nombre de tubes multiplié par 0·002 % donne directement la proportion d'oxyde de carbone dégagé.

Cette méthode inspirée de celle recommandée par Ogier et Kohn-Abrest pour le dosage de l'oxyde de carbone dans l'air, apporte la *certitude absolue* de la présence de l'oxyde de carbone dans les gaz provenant de l'attaque des aciers par le chlorure cuivrique ; elle nous a fourni des résultats comparables à ceux obtenus par la méthode à l'anhydride iodique, telle que nous l'avons appliquée. Les chiffres

obtenus par l'hémoglobine ont pourtant une légère tendance à être plus élevés que ceux donnés par l'anhydride iodique ; nous pensons que cela est dû à une saturation incomplète de l'hémoglobine, dont l'oxyde de carbone se trouve entraîné par le courant de gaz inerte. Le spectroscope nous a toujours indiqué en effet la présence d'une faible quantité d'hémoglobine oxygénée, dans tous nos tubes. Néanmoins, nous tenons à signaler cette méthode de contrôle, qui nous permet d'affirmer que l'iode que nous avons obtenu est bien réellement attribuable à la réduction de l'anhydride iodique par l'*oxyde de carbone*.

L'oxyde de carbone ne semble d'ailleurs pas être formé pendant l'attaque, par l'altération d'autres produits carbonés ; car sa proportion reste sensiblement constante dans les *aciers usuels ;* elle se tient aux environs de 0·013 % pour toute teneur en carbone supérieure à 0·30 %, et se montre, par conséquent, à partir de cette limite, tout à fait indépendante de la proportion de carbone contenue dans le métal.

Discussion on the Detection and Estimation of Rare Metals in Minerals. Particularly in connection with such as are used in :—

(1) The Manufacture of Special Steels, and

(2) Of Incandescent Mantles.

Mr. George T. Holloway opened the discussion by pointing out the great cost and the enormous increase in the use of the rare metals, many of which were only prepared or known as scientific curiosities a few years ago, but are now employed by the ton, and the necessity for more accurate methods of detecting and estimating them.

Published methods of analysis are often vague and inconclusive, and even the best are liable to break down and to yield entirely incorrect results when applied to a mineral. They have usually been worked out on prepared mixtures, but have, as a rule, not been carried sufficiently far to adequately cope with the eccentricities of Nature. At the present time both the analyst and the manufacturing chemist or metallurgist require more accurate and quicker methods

of determining the composition of rare minerals, and are particularly in need of reliable *qualitative* tests, without which correct quantitative determinations are impossible even with the best of our present methods. In minerals, we naturally find such metals associated as have more or less similar properties, and therefore require especial care in their identification and separation; and we also find unexpected associations which, unless recognised and properly dealt with, render even standard methods unreliable and often worthless.

Owing to the fact that many rare minerals are unsaleable unless separated from certain associates, which generally necessitates the use of special dressing appliances or other methods of treatment, and in view of the heavy losses which occur during such separation, methods of detecting and determining *traces* of a rare mineral in presence of large quantities of other rare minerals or waste matter are becoming of increasing importance. An error of a quarter of a per cent. may often be ignored in the analysis of a concentrate, but methods are in common use for many rare metals which fail to show even half the real losses in waste matter or "tailings," and which thus totally fail to indicate where improvements should be aimed at in the preparation of minerals for the market. On the other hand, these "standard" methods yield abnormally high results in the case of waste products or low-grade minerals from a few mines, on account of the presence of traces of rare metals which—usually absent in such ores—happen to be associated with them in that locality. Such associations, which are particularly dangerous in the case of rare minerals, afford another reason for the discovery and application of reliable qualitative tests.

The speaker was of opinion that volumetric and colorimetric methods may be found by which, after a preliminary and comparatively easy separation of a metal as an impure oxide or salt, it may be determined accurately without passing through a tedious and often very imperfect separation from the other metals which become collected with it in such preliminary separation.

The estimation of tungsten was mentioned as typical of some of the difficulties which met one in the case of rare minerals. Not only is wolfram (and, similarly hübernite, scheelite and other of the tungsten minerals) valuable when the ore can be picked or dressed to the required standard, but it is highly objectionable when present in tin and other ores as prepared for sale. In Cornwall alone, notwithstanding the introduction of the magnetic separator, which has

permitted the separation of wolfram from tin ore to an extent scarcely dreamed of ten years ago, the speaker estimated that between 120 and 150 tons of wolfram is still presented annually to the tin smelter as an impurity in the tin ore. Many thousands of pounds are thus lost annually by the mine-owners. A large proportion of this could be recovered, and there is reason to hope that a method of analysis recently introduced by Mr. H. W. Hutchin will show the ore dresser which part of the dressing process or plant requires most careful watching.

Minerals containing tungsten, molybdenum, vanadium, tantalum, niobium, uranium, etc., are now in demand for hardening steel and for other purposes, and although in a few cases the demand may prove evanescent, the probability is that the call for most of the metals and oxides yielded by these minerals is permanent.

The speaker, twenty years ago saw molybdenite being employed for blacking grates in one of the outports of Newfoundland, and created some disgust by proving it not to be graphite. At that time almost worthless, it can now be sold for steel-hardening purposes at from £120 to £150 per ton of 2,240 lbs., if free from gangue.

The necessity for some good method of analysis of tantalite is shown by the fact that the speaker was, about a year ago, connected with a dispute in which two analysts, experienced in analysis of tantalite, respectively reported 62 per cent. and 45 per cent., while the referee reported 35 per cent. of tantalic acid.

Even in the case of uranium, there are many pitfalls, although they are largely matters which those who are experienced in uranium can avoid. A method of analysis which yields satisfactory results with one variety of pitchblende, will fail on another apparently similar sample. Vanadium and phosphoric acid interfere with certain methods, as is well known, but there are other matters requiring elucidation, and the advisability of making a preliminary qualitative examination of a sample of uranium ore, whether pitchblende, uranite or other variety, is as great as is the case with minerals of other rare metals.

The history of the monazite trade shows how demand creates supply, and the extensive literature which has been published on the subjects of the rare earths used for the manufacture of incandescent mantles, and for similar purposes, shows how great and successful has been the attention devoted to the subject. Much room for improvement still exists, however, even in this branch of work, and the

introduction of thorianite and other thorium minerals into the incandescent mantle trade has further widened the field for research.

Another important mineral is the one from which lithia is now mainly prepared—amblygonite—a hydrated phosphate of aluminium and lithium. Large quantities of this mineral, containing probably 7 per cent. of lithia, were sold from one mine as inferior phosphate for manurial purposes. The purchaser's knowledge diverted it to its proper use, much to his pecuniary benefit, but the seller only learnt the fact by accident. Even now, the published methods of determining lithia are most unsatisfactory for this mineral.

The speaker considered that the subject under discussion was one of pressing importance, and that, among the matters mentioned as deserving attention, the discovery of reliable qualitative tests, and particularly of methods for identifying and estimating traces of these rare metals, were the most urgent. He particularly pointed out that the identification and determination of rare metals in *minerals* was distinctly different from the testing of the metals or *products* from the minerals or of the alloys in whose manufacture such metals have been employed.

Mr. H. W. Hutchin said:—Mr. Holloway has drawn attention to the breakdown of standard methods when applied to a mineral or natural mixture of minerals. The determination of tungstic acid in Cornish tin-wolfram ores is an instance coming within the speaker's experience. These ores contain from $1\frac{1}{2}$ to 2 per cent. of SnO_2; 0·5 per cent. WO_3 as wolfram, ·25 % Cu as sulphides along with the lode minerals—quartz, felspar, tourmaline, chlorite, and fluorspar, the latter often in considerable quantity. The aqua regia method was unreliable, giving low results; no better results were obtained when the ore charge was cleaned with hydrofluoric acid. The solubility of WO_3 in aqua regia is increased by the presence of arsenates and fluorides. Fusion with alkalies followed by the well-known mercury method gave good results, but the time taken for a single determination was so long as to render its use impracticable for technical purposes.

Wolfram may be completely decomposed by digestion with caustic soda solution. For details of application of this reaction to the determination of WO_3, followed by the usual mercury method, refer to Bulletin 56, Institute of Mining and Metallurgy.

New apparatus for the rapid electro-analytical separation of Metals.

By Henry J. S. Sand.

The apparatus described by the author (Trans. Chem. Soc., 1907, *91*, 373, and 1908, *93*, 1572) which first combined in a practical manner very vigorous stirring of the electrolyte with the possibility to measure the potential of the cathode by means of an auxiliary electrode, has been further developed especially with the view to make it more portable and readily set up.

It has been made possible to transport the electrolytic stand without taking out the mercury, making electrical connection between the stationary and movable parts, by providing a specially designed cap which may be screwed down when the stand is not in use.

A friction-clutch arrangement has been designed by means of which it is possible to throw the stirring arrangement in and out of gear with the motor without stopping the latter. Such an arrangement is useful when it is desired to run several apparatuses from one shaft driven by a single motor, or when a small motor-generator is employed for the double purpose of stirring and supplying the current; or, lastly, when a water or hot-air motor is employed which cannot be stopped readily while the electrodes are being washed.

The electrical apparatus for measuring the potential of the cathode, consisting of a sliding rheostat, a volt-meter and a capillary electrometer with its tapping key has been connected up in a single potentiometer-box; and a second tapping key is also provided, on depressing which the volt-meter indicates the potential between the anode and the cathode directly on a second scale.

For the purpose of the potentiometer-box a special new form of portable capillary electrometer has been designed which may be described briefly as an enclosed form developed from the Ostwald horizontal capillary electrometer.

De l'Influence de la Tension superficielle sur les Indications des Aréomètres.

Par M. B. Delachanal,

Chef des Travaux chimiques à l'École Centrale des Arts et Manufactures, Paris.

La première partie de ce travail a consisté à déterminer les tensions superficielles de dissolutions sucrées très fortement colorées et très visqueuses. Les procédés généralement utilisés pour faire ces déterminations ne convenaient pas, les lectures étant presqu'impossibles au travers de dissolutions à peu près complètement opaques et très épaisses. Pour tourner ces difficultés j'ai dû imaginer l'appareil suivant dans lequel j'ai déterminé au moyen de la balance les efforts exercés sur une lame de métal par le mouillage. Il se composait essentiellement d'une lame métallique enroulée en un cylindre incomplètement fermé et plongeant de 10 millimètres dans le liquide en expérience. L'instrument étant au préalable équilibré sur le côté gauche de la balance perdait par immersion un poids très faible à cause du liquide déplacé, et au contraire il était sollicité bien plus énergiquement par l'ascension du ménisque.

L'action exercée sur le fléau de la balance était compensé au moyen de poids, et il suffisait d'ajouter au poids ainsi obtenu celui du liquide déplacé pour avoir celui qui correspondait exactement à l'effort dû à la capillarité.

Pour les liquides simples, comme l'eau, la benzine, il était facile d'arriver à un équilibre persistant : il en était de même pour l'huile de vaseline, malgré sa viscosité assez grande ; pour les solutions sucrées au contraire l'équilibre était absolument momentané. Le plateau contenant les poids l'emportait et il fallait le décharger pour ramener l'équilibre ; celui-ci d'ailleurs n'était pas plus définitif que le précédent. Il nous a été impossible d'arriver, en suivant l'opération pendant douze heures, à un terme absolument constant.

On pourrait croire que cette impossibilité d'arriver à un équilibre définitif est dû à l'écoulement très lent de la liqueur sucrée sur la paroi de la lame métallique qui est mouillée au-dessus du ménisque. Mais il n'en est rien, car la lame de métal, plongée dans le liquide par un dispositif spécial de la balance à la même hauteur que la première fois, revient très rapidement au dernier état d'équilibre constaté. Il semble donc qu'il y a là une polarisation spéciale de la lame et du liquide qui ne cesse que lorsque celle-ci a été lavée et séchée ; alors une nouvelle expérience conduit à une dégradation de l'effort de capillarité absolument semblable au précédent.

Cette dégradation a été observée pour d'autres solutions ne contenant pas de matières organiques.

Nous ne devons pas exagérer l'importance de ce phénomène spécial ; même pour la solution de sucre pur, où il a plus d'importance que pour les solutions de mélasse, il ne conduit dans les lectures faites sur l'aréomètre Brix qu'à des différences assez faibles, quelques centièmes de degrés seulement.

On trouvera dans les trois tableaux ci-joints les valeurs de la tension superficielle des solutions de sucre pur et de mélasses obtenues par ce procédé.

TENSION SUPERFICIELLE DES SIROPS DE SUCRE PUR.

Brix.	Tension initiale.	Tension après 20 minutes.	Tension moyenne.	Brix.	Tension initiale.	Tension après 20 minutes.	Tension moyenne.
0	23·6	23·6	23·6	17	23·2	20·8	22·0
1	23·6	23·3	23·4	18	23·2	20·7	21·9
2	23·5	22·9	23·2	19	23·1	20·6	21·8
3	23·5	22·7	23·1	20	23·0	20·6	21·8
4	23·5	22·5	23·0	21	23·0	20·6	21·7
5	23·5	22·3	22·9	22	22·9	20·5	21·7
6	23·5	22·1	22·8	23	22·8	20·5	21·6
7	23·4	22·0	22·7	24	22·7	20·5	21·6
8	23·4	21·8	22·6	25	22·5	20·5	21·5
9	23·4	21·6	22·5	26	22·4	20·5	21·4
10	23·4	21·5	22·4	27	22·2	20·5	21·3
11	23·3	21·4	22·3	28	22·0	20·5	21·2
12	23·3	21·3	22·3	29	21·9	20·5	21·2
13	23·3	21·1	22·2	30	21·8	20·5	21·1
14	23·3	21·0	22·1	31	21·7	20·5	21·1
15	23·3	20·9	22·1	32	21·6	20·6	21·1
16	23·2	20·8	22·0	33	21·6	20·6	21·1

TENSION SUPERFICIELLE DES SIROPS DE SUCRE PUR—*continuation.*

Brix.	Tension initiale.	Tension après 20 minutes.	Tension moyenne.	Brix.	Tension initiale.	Tension après 20 minutes.	Tension moyenne.
34	21·5	20·6	21·0	45	22·3	21·2	21·7
35	21·5	20·6	21·0	46	22·4	21·3	21·8
36	21·5	20·7	21·1	47	22·5	21·3	21·9
37	21·6	20·7	21·1	48	22·6	21·4	22·0
38	21·6	20·8	21·2	49	22·7	21·5	22·1
39	21·7	20·8	21·2	50	22·9	21·6	22·2
40	21·8	20·9	21·3	51	23·0	21·6	22·3
41	21·9	21·0	21·4	52	23·1	21·7	22·4
42	22·0	21·0	21·5	53	23·2	21·8	22·5
43	22·1	21·1	21·6	54	23·4	21·9	22·6
44	22·2	21·1	21·6	55	23·5	22·0	22·7

TENSION SUPERFICIELLE DES SOLUTIONS DE MÉLASSES DE BETTERAVES.

Brix.	Tension initiale.	Tension après 20 minutes.	Tension moyenne.	Brix.	Tension initiale.	Tension après 20 minutes.	Tension moyenne.
0	23·6	23·6	23·6	23	17·0	16·1	16·5
1	20·5	19·4	19·9	24	17·0	16·0	16·5
2	19·9	18·6	19·2	25	16·9	15·9	16·4
3	19·5	18·3	18·9	26	16·8	15·9	16·3
4	19·2	18·1	18·6	27	16·8	15·8	16·3
5	19·0	18·0	18·5	28	16·7	15·6	16·2
6	18·8	17·8	18·3	29	16·7	15·6	16·1
7	18·6	17·7	18·1	30	16·6	15·5	16·1
8	18·5	17·6	18·0	31	16·5	15·5	16·0
9	18·3	17·4	17·8	32	16·5	15·4	15·9
10	18·2	17·3	17·7	33	16·4	15·4	15·9
11	18·1	17·2	17·6	34	16·4	15·3	15·8
12	18·0	17·1	17·5	35	16·3	15·2	15·7
13	17·9	17·0	17·4	36	16·3	15·2	15·7
14	17·8	16·9	17·3	37	16·2	15·1	15·6
15	17·7	16·8	17·2	38	16·2	15·0	15·6
16	17·6	16·7	17·1	39	16·1	15·0	15·5
17	17·5	16·6	17·0	40	16·1	14·9	15·5
18	17·4	16·5	16·9	41	16·0	14·9	15·4
19	17·3	16·4	16·8	42	16·0	14·8	15·4
20	17·3	16·3	16·8	43	16·0	14·8	15·4
21	17·2	16·2	16·7	44	15·9	14·7	15·3
22	17·1	16·2	16·6	45	15·9	14·7	15·3

TENSION SUPERFICIELLE DES SOLUTIONS DE MÉLASSES DE CANNES.

Brix.	Tension initiale.	Tension après 20 minutes.	Tension moyenne.	Brix.	Tension initiale.	Tension après 20 minutes.	Tension moyenne.
0	23·6	23·6	23·6	26	16·2	14·8	15·50
1	20·0	17·5	18·80	27	16·2	14·8	15·45
2	18·7	16·8	17·70	28	16·1	14·8	15·45
3	18·3	16·4	17·30	29	16·1	14·8	15·45
4	18·0	16·2	17·10	30	16·1	14·8	15·45
5	17·7	16·0	16·80	31	16·1	14·8	15·40
6	17·5	15·8	16·65	32	16·1	14·8	15·40
7	17·4	15·7	16·50	33	16·1	14·8	15·40
8	17·2	15·6	16·40	34	16·1	14·8	15·40
9	17·1	15·5	16·30	35	16·1	14·8	15·40
10	16·9	15·4	16·15	36	16·1	14·8	15·40
11	16·8	15·4	16·10	37	16·1	14·8	15·40
12	16·7	15·3	16·00	38	16·1	14·8	15·45
13	16·6	15·2	15·90	39	16·1	14·8	15·45
14	16·6	15·2	15·85	40	16·1	14·8	15·45
15	16·5	15·1	15·80	41	16·1	14·9	15·45
16	16·4	15·1	15·75	42	16·1	14·9	15·45
17	16·4	15·1	15·70	43	16·1	14·9	15·50
18	16·3	15·0	15·65	44	16·1	14·9	15·50
19	16·3	15·0	15·60	45	16·2	15·0	15·55
20	16·3	14·9	15·60	46	16·2	15·0	15·55
21	16·3	14·9	15·60	47	16·2	15·0	15·60
22	16·2	14·9	15·50	48	16·2	15·1	15·60
23	16·2	14·9	15·50	49	16·2	15·1	15·65
24	16·2	14.8	15·50	50	16·2	15·1	15·65
25	16·2	14.8	15·50				

J'ai supposé que l'aréomètre de Brix est dressé dans des sirops de sucre. Cela paraîtra tout naturel et il aura au moins l'avantage d'être exact dans le cas où il s'agit de déterminer la richesse saccharine de sirops à peu près purs.

Quand on emploie cet instrument ensuite pour l'essai des sirops impurs on déduit des lectures après plongées la richesse apparente de ces sirops plus ou moins étendus. C'est là où l'on commet une erreur, car la tension superficielle des égouts étendus est bien inférieure à celle des sirops purs correspondants. L'erreur ensuite est multipliée pour avoir la richesse apparente par un nombre généralement voisin de trois.

La tension superficielle des solutions de mélasses étant moindre

que celle des solutions de sucre c'est comme si l'on enlevait du poids au Brix employé ; il remonte et accuse un degré trop fort.

En fait, l'erreur ainsi commise est absolument variable avec l'aréomètre dont on se sert ; elle est en raison inverse du volume situé au-dessous de la surface de la liqueur et en raison directe du diamètre de la tige. On comprendra donc qu'il est impossible de donner à priori une valeur exacte à cette erreur ; elle varie suivant les conditions de l'expérience.

Cependant pour fixer les idées et pour faire comprendre que son importance n'est pas négligeable je puis dire qu'elle est très approximativement d'un demi-degré pour un Brix dont la marche est de 10 millimètres par degré. Cette erreur sera encore sensiblement d'un degré pour un Brix de marche moins sensible et de deux degrés pour un Brix présentant seulement deux millimètres et demi d'écart par degré.

Il conviendrait donc pour la détermination de la richesse apparente des sirops d'égout, qui a son importance dans le travail des sucreries, de fixer d'abord la base de la graduation des Brix utilisés et ensuite les dimensions principales de cet aréomètre

Sulla determinazione dello Zolfo per Via Catalitica.

Di G. Maderna.

Il metodo Brunck, il quale per primo ha utilizzato l' azione catalizzatrice dell' ossido di cobalto per determinare lo zolfo totale nei combustibili, può convenientemente essere impiegato in sostituzione del metodo Eschka per la determinazione di tale elemento nei carboni, purchè si prendano alcune precauzioni. Come l'ossido di cobalto può essere pure utilizzato l' ossido di nikel che sul primo presenta qualche vantaggio. Tale metodo viene applicato con successo alla determinazione dello zolfo nelle piriti e nei bitumi. Per questi ultimi si sentiva veramente e da tempo la mancanza di un metodo pratico ed esatto. Di tutti i metodi finora proposti per dosare lo zolfo in tali sostanze i soli che possono essere (quantunque non sempre) impiegati sono il metodo Eschka modificato ed il metodo Henriques. Sopra questi il metodo di dosamento per via catalitica, oltre all' esattezza, presenta il grande vantaggio della rapidità, colla quale si giunge al risultato finale.

Sulla Precipitazione del Fosfomolibdato Ammonico in presenza di Acidi organici.

Di G. Maderna.

L'azione esercitata dai varii acidi organici sulla precipitazione dell' acido fosforico come fosfomolibdato ammonico è poco conosciuta. Numerose esperienze eseguite a questo proposito portano alle seguenti conclusioni principali: I° Contrariamente a quanto sostiene Hundeshagen gli acidi organici non impediscono la precipitazione del fosfomolibdato ammonico, quando siano presenti nella soluzione quantità sufficienti di acido nitrico. II° Una precipitazione quantitativa dell' acido fosforico per mezzo del molibdato ammonico è possibile anche semplicemente in presenza di taluni acidi organici (fra questi l'acido tartarico e l'acido ossalico), purchè vi sia un determinato rapporto fra tali acidi organici ed il reattivo determinante la precipitazione. III° I composti organici che si formano certamente fra acido molibdico e forte acido fosforico da una parte ed acidi organici dall' altra sono abbastanza stabili: essi devono essere a costituzione non omogenea, o, se lo sono, complessi a prodotto di solubilità superiore a quello del fosfomolibdato ammonico.

The Detection of Mercury by Toxicological Analysis of Volatile Poisons.

By Marco T. Lecco.

Next to arsenic the most frequent cases of poisoning are due to mercury and the compounds of mercury. Metallic mercury is not a poison unless it is in the form of vapour or otherwise distributed in a very fine form, and all compounds of mercury are not poisons. It is known, for instance, that mercury sulphide is not poisonous.

In the usual method of examination for mineral poisons, the intestines and other objects are commonly destroyed by hydrochloric acid and potassium chlorate, and in this and similar cases mercury and all compounds of mercury, if they are present, dissolve at the same time. Because of this it is not possible to recognise in which

form mercury eventually presents itself in the object tested, and it is also impossible to tell if the discovered mercury was employed in a form in which it was able to act as a poison, or in any other form. Poisonous compounds of mercury decompose very easily under the influence of animal and vegetable matter, and, therefore, cannot be isolated after a certain time has elapsed.

About twenty years ago, on the occasion of a chemical-judicial analysis of volatile poisons, I remarked that mercury could be distilled with water far more easily than had hitherto been thought possible. Mercury which has been distilled with water appears in the distillate either as a very fine skin on the surface of the distillate, or in the form of very fine, sometimes almost invisible, suspended particles, or in tiny drops on the bottom of the vessel. If mercury is present in any form in the distillate, we can recognise it if we leave it to itself for some days or immediately filter it, and wash the filter with water, alcohol and ether. If any mercury remains on the filter it appears in characteristic, glittering metallic drops, which can be seen without the magnifying glass if the quantity is not too small. In this manner it is not possible to prove mercury if we mix it or mercury sulphide with intestines or other animal or vegetable matter and distil with water as we usually do in the analysis of volatile poisons. On the contrary, if we mix poisonous compounds of mercury, *e.g.*, sublimate with animal or vegetable matter with water and distil, the mercury appears in the distillate in remarkable quantities. Through the influence of the above-mentioned organic bodies the sublimate and also calomel are reduced, on boiling, to metallic mercury, and in that way precipitated mercury is distributed in the finest particles. Mercury distils with water in remarkable quantities if it is in as fine a form as we obtain it by precipitation of a diluted solution of sublimate in water with stanous-chloride. The appearance of mercury in the distillate in the toxicological analysis of volatile poisons can also serve as a proof of the presence of mercury in the form of compounds, which reduce easily when they come into contact with animal or vegetable stuffs, or else of mercury in a state of very fine division. In both these cases the mercury is present in a poisonous form. Therefore, mercury can be added to the group of volatile poisons in the systematic chemical-judicial analysis of poisons.

On the disturbing effect of Alcohol in the detection of Volatile Poisons.

By Marco T. Lecco.

Phosphorus or phosphorous acid is generally looked for in the distillate obtained when testing for volatile poisons, in chemico-legal analyses, a part of the distillate being oxidised with chlorine or nitric acid and heated on the water bath as long as necessary.

Once when oxidising with nitric acid I obtained very fine crystals, which were well developed, colourless, prismatic, and which turned out to be oxalic acid. It was interesting to find out how this oxalic acid was formed. In the distillate from intestines, different putrid products of decomposition of animal matter are usually present. I have, however, examined a great number of intestines, and never noticed the formation of oxalic acid through the action of nitric acid on the volatile part of the products of decomposition of the organic matter.

If these products produce oxalic acid by oxidation, this acid ought always to appear. When I obtained oxalic acid I found that alcohol was present in the intestines which were being examined, and always as I evaporated a dilute solution of alcohol with water, I obtained fine crystals of oxalic acid. Therefore alcohol may be present when crystals of oxalic acid are obtained on oxidising the distillate with nitric acid for the examination of volatile poisons.

The Determination of Lithium in Water.

By Marco T. Lecco.

Lithium is regarded as a rare element, the determination of it in mineral water being complicated; it is not looked for in every water. I know of no attempt which has been made to determine lithium in the filtrate from magnesium-phosphate, but certainly many more waters would be examined for lithium if it were possible to use the above for its determination.

In technical analyses more attention would be paid to the rarer elements if their qualitative and quantitative determinations were included in the usual systematic method employed for the better known elements. In the filtrate from magnesium-phosphate lithium is in solution. It is determined by evaporating in a platinum basin over a water bath, and after drying the residue by heating to over 100° C., and then treated by the method proposed by W. Mayer and recommended by Fresenius. If a clear solution is obtained there is no lithium in the water, or the quantity is very small. Generally a more or less cloudy solution is obtained, often on account of the reagents not being pure enough, or from products of the reaction on the glass vessels. The qualitative reaction shows the composition of the above precipitate, and whether it contains lithium. By the above-mentioned method, I carried out several comparative analyses of one kind of Servian alcaline water, acid water with about 2 grams. dry substance, and 2·5 grams. free carbonic per litre, to which different quantities of lithium chloride solution were added.

Although I did not always receive satisfactory results, I am convinced that, under certain conditions, it would be possible in the above-mentioned way to determine lithium in mineral water, and, as the following examples show, it is also possible to obtain sufficiently exact results:—

	gr. SiO_2	gr. $\frac{Al_2O_3}{Fe_2O_3}$	gr. CaO	gr. MgO	gr. Li_2O found.	gr. Li_2O added.
In 100 cc. Mineral Water:						
Without Lithium ...	0·050	0·006	0·0232	0·0254	trace	0
With 0·06686 gr. Lithium	0·048	0·005	0·0232	0·0254	0·0243	0·0236
With 0·03343 „	0·050	0·006	0·0238	0·0253	0·0115	0·0118

I think the above-mentioned way of determining lithium in water would have a certain value. Not only would it give the impulse to search for and determine lithium in every water analysis in addition to calcium and magnesium determination, but perhaps would also provoke further research and development of the method of the determining of lithium in water, with which Fresenius Ramelsberg and other well-known chemists have occupied themselves.

Mr. A. Chaston Chapman remarked that it would be a great

advantage if water analysts would more frequently examine waters they had under examination for the presence of the so-called rarer elements. He had on several occasions detected distinct traces of lithium and even rubidium in waters which had been often analysed and never suspected of containing those elements.

Estimation of Sodium Cyanamide and Nitrolim.

By FRANK E. WESTON, B.Sc., and H. RUSSELL ELLIS, B.Sc.

In estimating cyanamide in sodium cyanamide and nitrolim discordant results were obtained when the method was varied. The methods used were: (1) The estimation of N in nitrolim by the Kjeldähl process, as described in the "Principles and Practice of Agricultural Analysis," Fertilizers and Insecticides, Vol. II., p. 311, 1908 ed., by Wiley, "the best way to determine the nitrogen in calcium cyanamide is to digest it with strong sulphuric acid by the usual Kjeldahl process," and the Estimation of Cyanamide, by R. Perotti, J. C. S., Abs. II., 870, 1905. The latter method consists of running a cyanamide solution from a burette into a known volume of $\frac{N}{10}$ $AgNO_3$ rendered distinctly alkaline, but not excessively so, with ammonia, leaving an excess of $AgNO_3$ in solution. The precipitate is coagulated by gently warming and shaking, then filtered and the filtrate titrated against $\frac{N}{10}$ NH_4CNS to find the excess of $AgNO_3$. The difference in the amount of $AgNO_3$ taken and that found in filtrate is calculated as cyanamide. Perotti states that this method can also be used in estimating the cyanamide in nitrolim. Now it is quite evident that the Kjeldahl method will give the total N in the substance, whether it is as cyanamide, cyanide, nitride, or other complex N compounds; consequently, the results will be higher than results obtained by estimating the cyanamide only. In Perotti's method the following errors are likely to occur:—

(1) Too large an amount of NH_4OH solution on warming dissolves a small amount of the Ag_2 CN_2.

(2) All the AgCN precipitated is not dissolved by the NH_4OH,

and hence ppt. consists of AgCN and Ag_2CN_2; moreover, when the $AgNO_3$ in excess is estimated by Volhard's method, the AgCN in solution is precipitated, and thus introduces an error.

(3) Any chloride or sulphide in the original substance also interferes in a similar way.

In order to avoid these errors several experiments were carried out with a view to eliminate the error due to cyanide in the sodium cyanamide used, and finally the following method was adopted. A solution of sodium cyanamide of approximately $\frac{N}{10}$ strength was prepared, and 20 ccs. of this solution was added to 40 ccs. of $\frac{N}{10}$ $AgNO_3$, and 10 ccs. of N HNO_3; a ppt. of AgCN was obtained. The solution was filtered, and the filtrate allowed to flow into 20 ccs. of N NH_4OH; the washings also were collected in the same solution. A yellow ppt. of Ag_2CN_2 was obtained in the ammonia solution; this was gently warmed in order to coagulate the ppt., filtered, and well washed. The AgCN ppt. was washed into a flask, and well boiled with HNO_3 to expel all HCN, and the resulting $AgNO_3$ estimated with $\frac{N}{10}$ or $\frac{N}{50}$ NH_4CNS, using $Fe_2(SO_4)_3$ as indicator. The Ag_2CN_2 ppt. was treated on the filter paper with cold dilute HNO_3 (1 of con. acid to 5 of water), and the filter paper well washed with cold water to dissolve out all the $AgNO_3$ formed, and the $AgNO_3$ estimated by Volhard's process.

It was found that very concordant results could be obtained if the following precautions were observed:—

(1) The solutions should not be left for any length of time in contact with HNO_3, as the latter slowly decomposes the cyanamide into urea.

(2) The solutions should not be boiled, as this slowly decomposes the cyanamide.

Experimental.

The sodium cyanamide used in these experiments was Kahlbaum's. It was a white fibrous substance, crystalline and hard under the outer coating, the inner portions were darker than the surface; the change was evidently due to atmospheric action.

The substance was easily powdered, and was very soft under the pestle, easily soluble in water, with a hissing noise and much evolution of heat, a slight evolution of gas was observed on adding water. The resulting solution was strongly alkaline.

The solution did not smell of NH_3, nor even after prolonged boiling; after well boiling with NaOH the smell of NH_3 was observed.

Effect of Acids.

(1) *Dilute HCl.*:—Easily soluble with heat evolution, and formation of a pink coloration discharged by excess of acid. Colour was probably due to a slight trace of sulphocyanide and iron; the smell of HCN was noticed.

(2) On boiling with any dilute acid for a short time the whole of the cyanamide was destroyed in some cases with the formation of urea. With HNO_3 the yield of urea was almost theoretical as demanded by the equation.

$$Na_2CN_2 + H_2O + 2\,HNO_3 = 2\,NaNO_3 + CO(NH_2)_2.$$

(3) *Test for Cyanide:*—

(*a*) A small quantity of the solution boiled with NaOH, $FeSO_4$, and $FeCl_3$, cooled and HCl added, a copious ppt. of prussian blue was obtained.

(*b*) Another portion boiled with dilute H_2SO_4 for half-hour, and the test carried out as (*a*), only a very faint prussian blue ppt. obtained, showing that the HCN had been expelled.

(4) *$KMNO_4$ Solution.*—When a solution of Na_2CN_2 is added to a solution of $KMNO_4$, a green coloration is immediately produced, and after a time a brownish precipitate.

I. *Typical estimation* of Na_2CN_2 by Perotti's method:—

1·9716 gms. of sodium cyanamide treated with water, filtered from insoluble matter, and made up to 250 ccs.

No. of Estimation.	Vol. of Na_2CN_2.	Vol. of $\frac{N}{10}$ $AgNO_3$.	Vol. of N NH_4OH.	Vol. of NH_4 CNS used for excess of $AgNO_3$ in filtrate.	Vol. of $\frac{N}{10}$ NH_4 CNS used for $AgNO_3$, obtained from Ag_2CN_2 by HNO_3.
1	10 c.cs	20·06 c.cs	10 c.cs	3·85 c.cs	15·88 c.cs
2	10 „	20·28 „	20 „	4·35 „	16·00 „
3	10 „	20·06 „	50 „	4·21 „	15·83 „

From which % of Na_2CN_2 = 86·896 calculated from excess of $AgNO_3$, etc.

N.B.—(1) On adding HNO_3 to the filtrate from Ag_2CN_2 ppt., a white ppt. of AgCN was thrown down. (2) On dissolving Ag_2CN_2 in HNO_3 a white residue of AgCN was left.

II. *Typical estimation of Na_2CN_2 by author's method,* same solutions as in previous method.

No. of Estimation.	Vol. of Na_2CN_2.	Vol. of N. HNO_3 used.	Vol. of $\frac{N}{10}$ $AgNO_3$.	Vol. of NH_4 CNS $\frac{N}{100}$ for $AgNO_3$ from AgCN.	Vol. of N. NH_4OH.
1	10 c.cs	5 c.cs	20 c.cs	4·38 c.cs.	10 c.cs
2	10 „	5 „	20 „	5·3 „	10 „

Vol. of $\frac{N}{10}$ NH_4 CNS for $AgNO_3$ from Ag_2CN_2.	Vol. of $\frac{N}{10}$ NH_4 CNS for $AgNO_3$ in excess.
15·468	3·638
15·468	3·772

$^0/_0$ of $Na_2CN_2 = 84·456$ calculated from $AgNO_3$ obtained from Ag_2CN_2

$^0/_0$ of Na CN $= 3·011$.

III. *Effect of boiling aqueous solutions of sodium cyanamide:—*

Five ccs. of a known solution of cyanamide heated to boiling for a short time, run into 10 ccs. N NH_4OH, and excess $AgNO_3$, and washed free from $AgNO_3$, and then finally washed through the filter paper with cold dilute HNO_3, then with hot water, and finally titrated with $\frac{N}{10}$ NH_4CNS.

No. of Estimª.	Vol. of Na_2CN_2.	Time of boiling.	Vol. of NH_4 OH.	Vol. of $\frac{N}{10}$ NH_4CNS for $AgNO_3$ from Ag_2CN_2.	Vol. of NH_4CNS for Na_2CN_2 before boiling.
1	5 c.cs	20 m.ms	10 c.cs	8·58 c.cs	15·46 c.cs
2	5 „	35 „	10 „	6·29 „	15·46 „
3	5 „	60 „	10 „	3·05 „	15·46 „
4	5 „	90 „	10 „	1·6 „	15·46 „

IV. *Effect of hot HNO_3:—*

(1) Result of experiments carried out as in II., using hot solutions of HNO_3 and $AgNO_3$, *i.e.*, throwing out the AgCN from warm solutions of HNO_3 in order to save time during filtering.

Vol. of Na_2CN_2.	NHNO_3.	$\frac{N}{10}AgNO_3$.	$\frac{N}{10}NH_4CNS$ for AgCN.	NNH_4OH.	$\frac{N}{10}NH_4CNS$ for Ag_2CN_2.	$\frac{N}{10}NH_4CNS$ for excess $AgNO_3$.
10 c.cs	5 c.cs	20 c.cs	5 c.cs	10 c.cs	15·35 c.cs	3·77

Similar experiments showed that the results were concordant and as high as experiments carried out in the cold, if carried out quickly.

On boiling the Na_2CN_2 solution for 10 minutes with its own volume of N HNO_3, the silver cyanamide produced required 1·475 ccs. $\frac{N}{10}$ NH_4 CNS, instead of 15·46 ccs. for the total cyanamide present at first.

Result of allowing 10 ccs. of the sodium cyanamide to stand in the cold with 5 ccs. of N HNO_3:—

Expt.	Time.	$\frac{N}{10}NH_4CNS$ for Ag_2CN_2.	$^N NH_4CNS$ required if no change.
1	24 hours	14·95 c.cs	15·46
2	48 „	10·82 „	15·46
3	72 „	9·25 „	15·46

NITROLIM.

The sample used was supplied by J. J. Griffin & Co., and was contained in a tightly closed tin. It was a black powder, and smelt slightly of NH_3. On adding water a very slight smell of C_2H_2 was observed, but no gas was visibly evolved; the solution became warm. The aqueous solution on filtering from the black insoluble residue gave with ammoniacal $AgNO_3$ a thick yellow ppt. of Ag_2CN_2 which was soluble in HNO_3, leaving a white and black residue.

On adding HNO_3 to the solid H_2S was evolved in very slight quantity, and a very faint odour resembling mercaptan. The solution of the substances in HNO_3 gave with ammoniacal solution of $AgNO_3$ a yellow ppt. of Ag_2CN_2 and black Ag_2S and a white ppt. of AgCl.

No cyanide was found, although a fairly large quantity was used for the test.

The method of analysis was as follows: a sample of the finely powdered substance (1-2 gms.) is added to cold water and well stirred. This is filtered into a 500 c.c. flask and residue washed until a drop of the filtrate gave no reaction with ammoniacal $AgNO_3$ solution. The solution is made up to known bulk. 20 c.cs of this solution is run into a warm solution of excess of $AgNO_3$ and 20 c.cs N NH_4OH, the ppt. filtered and thoroughly washed with warm water. Dilute HNO_3 (1 con. acid to 5 water) is added to the ppt. in the filter paper and the filtrate and subsequent washings collected together. The silver in this solution is then estimated by Volhard's method. The sulphide and chloride present with the Ag_2CN_2 is not dissolved by the HNO_3, but remains on the filter paper.

V.—Typical estimation by this method:—

Expt.	Vol. of $CaCN_2$ Soln.	Vol. $\frac{N}{10}$ $AgNO_3$.	Vol. NNH_4OH.	Vol. NH_4CNS for $AgNO_3$ from Ag_2CN_2.	Vol. NH_4CNS for excess $AgNO_3$.
				B	A
1	20	20	20	8·85	10·7
2	20	20	20	8·80	10·625

% $CaCN_2$ calculating from A = 52·8 % (Perotti's method).
„ „ „ B = 46·88 % (Author's method).
$AgNO_3$ was ·09845N and NH_4CNS ·09558N
Wt. of nitrolim 1·8011 in 500c.cs.

VI.—Typical estimations by Kjeldahl.*

	Wt. of Substance.	Vol. NH_2SO_4 to collect NH_3.	Vol. of N.NaOH excess H_2SO_4.	Vol. N.NaOH equiv. to NH_3.
Expt. 1	·8974 gms	32·7 c.cs	21·399 c.cs	11·301c.cs
„ 2	1·494 „	32·7 „	14·29 „	18·41 „
„ 3	1·254 „	43·6 „	30·694 „	12·906 „

No. 1 gives 50·397 °/ₒ $CaCN_2$ estimating all N as $CaCN_2$.
„ 2 „ 49·3 „
„ 3 „ 50·131 „
Mean 49·94 „

Using method B as described under V. the following results were obtained:—

1.	°/ₒ $CaCN_2$	=	46·88
2.	„	=	46·85
3.	„	=	47·24
4.	„	=	46·89
5.	„	=	47·03
Mean	°/ₒ $CaCN_2$	=	46·98

Kjeldahl's method gives 2·96 per cent. $CaCN_2$ higher than the author's method, and this corresponds to 1·038 per cent. N. In order to find where the discrepancy arises the following experiments were carried out:—A weighed amount of nitrolim was dissolved in water filtered and well washed; the $CaCN_2$ in the filtrate was precipitated as $AgCN_2$ using excess of $AgNO_3$ (four times the weight of nitrolim used), again filtered, and the filtrate so obtained distilled with NaOH into standard H_2SO_4.

The residue from the nitrolim which was insoluble in water was treated as for a Kjeldahl estimation.

The following results were obtained:—

Expt.	Wt. of substance.	Vol. of NH_2SO_4 to receive NH_3.	Vol. of NH_4SO_4 for excess H_2SO_4.	Vol. $\frac{N}{10}$NaOH equiv. to NH_3.	°/ₒ N.
1	1·7964 gms.	A 11·027 c.cs	10·50 c.cs	5·27 c.cs	·411
		B 5·459 „	4·373 „	10·86 „	·847
			Total ...	...	1·258
		$\frac{N}{10}$	$\frac{N}{10}$	$\frac{N}{10}$	
2	2·765 gms.	A. 32·754 c.cs	27·2 c.cs	5·554 c.cs	·282
		B. 38·212 „	28·23 „	9·98 „	·532
					·814

A. Numbers for determination of NH_3 in aqueous filtrate from Ag_2CN_2.
B. „ for N is residue insoluble in water.

* Results are calculated for N. solutions—actual solutions used were approximately N or $\frac{N}{10}$.

VII.—Change of strength of solution of $CaCN_2$ on standing.

1·6077 gms. of nitrolim were dissolved in water as before and made up to 500 c.cs. This solution was well corked up and portions drawn off and estimated at stated intervals by method described:—

Expt.		Time of standing.	Vol. of nitrolim solution used.	Vol. N.NH_4OH solution used.	Vol. NH_4CNS solution for $AgNO_3$ from Ag_2CN_2.	
1	*a*	0 hrs. 0 mins.	10	10	4·05	= 4·075
	b	" "	10	10	4·125	
2	*a*	21 hrs.	20	20	4·00	= 4·01
	b	21 "	10	10	4·02	
3	*a*	45 "	20	10	7·85	= 3·95 for 10 c.cs
	b	45 "	20	20	7·95	
4	*a*	93 "	20	10	7·975	= 3·98
	b	93 "	20	7·5	8·00	

The nitrolim solution under the conditions above is only very slowly decomposed. After several days a very slight white deposit was formed.

VIII.—Variation in strength of a solution of $CaCN_2$ containing HNO_3.

·9765 gms. of nitrolim was dissolved in water, as before and HNO_3 added. Portions of this drawn off at known intervals of time and the $CaCN_2$ estimated by methods described:—

Expt.		Time.	Vol. of nitrolim solution.	Vol. N.NH_4OH added.	Vol. of NH_4CNS $\frac{N}{10}$ for $AgNO_3$ from Ag_2CN_2.	
1	*a*	0 hrs. 0 mins.	40 c.cs	20	9·725	9·715 c.cs
	b	" "	40 "	20	9·7	
2	*a*	21 hrs.	40 "	20	9·2	9·2 "
	b	21 "	40 "	50	9·2	
3		69 "	40 "	20	8·325	8·325 "
4		189 "	40 "	20	6·425	6·425 "
5		504 "	40 "	20	3·775	3·775 "

Conclusions.

1. Na_2CN_2 and $CaCN_2$ can be quickly and accurately estimated by the method described by the authors.

2. The method lends itself to examining the rate of change of cyanamide under varying conditions, especially in soils which may contain chlorides, sulphides, and nitrogen.

3. Perotti's method invariably gives high results.

4. Kjeldahl's method likewise gives high results, since all the N ground is returned as $CaCN_2$.

An improved apparatus for the rapid estimation of Specific Gravity.

G. D. MACDOUGALD, *Dundee*.

A series of standard liquids of known specific gravity is provided, preferably arranged in a definite order of gradation in glass receivers resembling test tubes. These are mounted upon a stand to enable observations to be made transversely through the tubes. A tubular device is provided, having a very thin walled terminal extension of small capacity adapted to offer as small resistance as possible to the conduction of heat between the liquid to be tested and the standards.

A small drop of the fluid to be tested is discharged from a minute hole at the end of the terminal extension at, say, a depth of 5 centimetres below the surface of a standard, preferably against the side of the tube next the observer. The end of this extension near the point of delivery is bent so as to deliver the liquid to be tested in a horizontal direction. A series of such drops may be required in different standards to ascertain in which of the standards the liquid under test does not rise or fall, in which case the specific gravity of the fluid under test is that of the standard. More frequently the fluid to be tested rises in one standard and sinks in the adjacent standard. When this happens the speeds of rise and fall indicate the gravity, and the accuracy depends upon the intervals between the standards. For fairly accurate work a difference of ·0005 (water = 1.) between standards is convenient. This permits of an accuracy of ·0002. The process is accurate for such a non-homogeneous fluid as milk in standards of common salt solution, the time for each observation being from five to seven seconds before the drop begins to break up. For homogeneous fluids the time of observation is much longer.

Discussion.

Mr. THOMAS JAMIESON stated that he had submitted this method to a severe test, by finding with scrupulous care the specific gravity of ten samples of milk by the ordinary method, and without calculating the results, proceeded to find the gravities by the new method, which requires no calculation. On calculating the gravities

by the ordinary method it was found that in four cases the results were identical; in two cases a difference of —·00025, in three cases a difference of —·0005, and in one case a difference of —·00075. The last one being the first tried without practice, it was repeated when the difference was reduced to—·0005. He did not consider that these differences should properly be applied to the new method, but rather to the ordinary method, considering the manipulation connected with it.

It is seldom that a process is introduced that combines absolute accuracy with great rapidity. The usual time that is taken with the finding of a specific gravity by the ordinary methods might be put at 15 minutes, or say, 1,000 seconds. Now he had found that the average time necessary for taking an absolutely accurate specific gravity by the new method is only 10 seconds.

Mr. Grant Hooper asked if the author had any experience of a general application of this method. There were cases where one had very small quantities of such substances as oils, turpentines, or turpentine substitutes where this method might be usefully applied. The speaker, however, imagined that this would entail a very wide range of standard solutions. Could the author state what number of such solutions he had found it necessary to keep available?

Professor W. Fresenius:—Es fragt sich ob bei dieser Methode nicht darin eine Fehlerquelle liegt, dass nur *ein* Tropfen benutzt wird, so dass eine geringe Inhomogenität der zu prüfenden Flüssigkeit genügt, um zu bewirken, dass der Tropfen nicht dem mittleren spezifischen Gewicht zu demselben entspricht.

On the expediency of appointing a General International Permanent Committee to secure Uniformity in Methods of Analysis, and in the Interpretation of Results.

R. R. Tatlock.

ABSTRACT.

There are few analysts who have not been haunted by the vision of establishing a comprehensive international system of uniform analytical methods, and probably there are fewer still who believe that it could be satisfactorily accomplished. This scepticism, however, although it has been a hindrance, has not been a barrier to progress, and no better demonstration of this could be found than the excellent work which has been done by the Commissions appointed at former Congresses, and notably the one the splendid record of whose labours constitutes the Seventh Volume of the Proceedings of the last Congress which had its meeting in Rome three years ago. That collection of reports represents an amazing amount of work, particularly in connection with the subject of the unification of methods of analysis of alimentary substances, and it will be agreed that the best thanks of this section are due to M. Andre of Paris, and to Professor Piutti of Naples, and their collaborateurs, for the valuable aid they have rendered in promoting and increasing our knowledge of processes for the scientific examination and valuation of food stuffs. We are also greatly indebted to the Commissions which have reported on uniform methods of determining lead, copper, antimony, arsenic, gold, silver and sulphur, on systematic sampling, on weights and measures, on volumetric analysis and on instruments, but the character of the work done in these departments was guaranteed in advance by its association with the names of Lunge, Malino, Wiley, Thorpe, and their distinguished colleagues in the investigations.

Although such excellent work has been done, the question remains whether the time has not arrived when its scope should be extended and its base widened so as to include every question that may arise in the chemical examination of all commercial articles from the receipt of the sample to the signing of the report. I believe there are chemists who hold that such a consummation as this would be as difficult to attain to as that of a universal language or a universal religion, but I think there are very few who would be inclined to call in question the opinion

that much mutual benefit would result from increased systematised and permanent inter-communication between the analysts of all countries with regard not only to systems or processes of analyses themselves, but to inferences which can legitimately be drawn from the results obtained. Hitherto the efforts made to arrive at unification have, as far as I am aware, been confined to analytical methods as such, and have not dealt with the interpretation of results, in which, in numerous instances, the views and practice even of eminent chemists are "wide as the poles asunder," with the consequence often that the profession of the analyst is discredited in the eyes of the public. The condition of matters in this respect at present may fairly be described as chaotic, and it is doubtful whether there is such inexcusable diversity of opinion, on common ground, among the members of any other similar body of men, unless it be politicians. A few concrete examples will serve to illustrate this—

There are not many subjects upon which more labour has been bestowed, and more elaborate treatises written, than the analysis of water, but the accuracy and refinement attained, and the indisputable results as far as figures are concerned, are frequently rendered valueless by their interpretation. Some analysts do not hesitate to give a report upon the suitability of a water for dietetic purposes, based entirely upon the results of the chemical analysis; others require, in addition, a bacteriological examination, and there are chemists who consider it absolutely necessary to make an examination with regard to the source and history of the water. There are analysts who assume that the nitric nitrogen, even when present in considerable proportion, is of little or no significance, but there are probably more who consider it a valuable indicator of possible danger. Then the question of the condition of a water such as that of a stream or tidal river, in relation to fish life, does not seem to be disclosed by any or all of these three forms of examination, and it has been found necessary to give these only a secondary place, and to resort to the determination of the amount of free oxygen, the rate of the absorption of oxygen by the organic matter present, and the facility with which the water absorbs oxygen from the atmosphere. There can be no doubt that in some cases the misinterpretation of the significance of nitric nitrogen in potable waters has given rise to serious consequences, and it would be of the greatest importance to have a decided and authoritative statement with regard to its import, if present in appreciable proportion.

Another subject on which there is much divergence of opinion as

regards the inferences from the results is vinegar. It has been the practice of some chemists to demand that the residual products of the acetous fermentation must be present before the article can be accepted as malt vinegar, which of course disqualifies distilled malt vinegar. There are not a few also who affirm that the source of the acetic acid in certain samples is wood, although this is merely an inference from their figures and not the result of a direct chemical test.

There are few questions with regard to interpretation of results that have given rise to more controversy than those relating to brandy, whisky, rum and gin, many analysts of eminence holding that a standard or limit based upon analytical figures is absolutely unsuitable, while others have no hesitation in adopting arbitrary standards for any or all of these. Even if such standards were suitable, and were adopted, they must necessarily be exceedingly low ones, and must give rise to the grossest sophistication of the genuine article by more or less characterless alcohol. These remarks apply to all the four subjects referred to.

Even at the present time there seems to be little unanimity on the part of analysts of butter, as to how the results in certain cases should be interpreted. Some have taken the position that although no single figure may prove admixture or adulteration, the relation or balance between two or more of the constituents may disclose it, and no doubt this would be a reasonable enough view if the ratios found were outside of experience with genuine butters, but this condition has not always been observed.

A further instance of want of uniformity in the interpretation of results, is that of the so-called fruit wines. There are chemists who demand that these non-alcoholic beverages shall have no other source, either wholly or partly, than the juice of the particular fruit whose name they bear. Others again are satisfied with what they call a substantial proportion of the particular fruit juice.

It is scarcely surprising that there should be such divergency of opinion with regard to what ought to be legitimately inferred from the figures of analysis, because in many instances no inference at all can be made. For example, we may have the very best brands of genuine Cognac brandy showing exactly the same composition, by analysis, as genuine high class Pot Still Malt Whisky, or even genuine Pot Still Jamaica Rum, and in such cases it would be impossible to state which was the one or the other, without tasting and smelling them, and only by these means can we determine to which the arbitrary standards for brandy, whisky and rum respectively are to be applied. Seeing that

chemical analysis may not be able to distinguish between the one or the other, it must be hopelessly impossible to determine the quality by its means.

Another example of this is butter, the best quality of which will often show less volatile acids than a very poor quality.

What I would plead for is the appointment of a General International Permanent Committee or Commission, to secure not only uniformity in methods of analyses, with which already great progress has been made, but also in the interpretation of results. The present Commissions would naturally be incorporated in this wider scheme.

That the Institution of Official Methods for Agricultural Analyses is undesirable unless subject to periodical revision.

By John Hughes, F.I.C.

Mr. Hughes said he did not propose reading a paper, as it was not necessary, but he wished to open a discussion on the above resolution:—

As those present were aware, the Board of Agriculture in this country had recently issued official instructions that the analyses made under the provisions of the existing Fertilisers and Feeding Stuffs Act of 1906 were to be made according to special prescribed methods. Bearing in mind the wonderful improvements in methods of analyses that were being constantly brought forward, it seemed very undesirable to prescribe particular methods for making official analyses, because every one knew how difficult it would be to obtain official consent to any alteration in such methods.

No doubt under the original Act of 1893, the sellers of fertilisers and feeding stuffs, were exposed to frivolous and unjust criminal prosecution, based upon the analysis of an incompetent or careless local analyst, but such cause of complaint was now quite removed, because under the new Act of 1906 no prosecution could be instituted upon the certificate of the local analyst, but it is now necessary to obtain the consent of the Board of Agriculture, and such consent is not to be given until the third portion of the officially drawn sample has been submitted to the Chief Analyst in London.

Therefore there was absolutely no necessity for prescribing official methods of analysis, because the institution of legal proceedings of a criminal nature depended entirely on the analysis and advice of the Chief Analyst.

As regards these official methods, they appeared to be more tedious, and probably, when employed by careless or inexperienced operators, may yield more varying results than those obtained by the present methods, which are certainly quicker and more simple.

Why therefore should the numerous local analysts, who have hitherto obtained on the whole very close and reliable results, be obliged, upon the command of a non-scientific body like the Board of Agriculture, to adopt new methods of analyses, the accuracy of which is not assured and which are certainly likely to be improved or entirely superseded by new processes in course of time.

As the competence and reliability of the Chief Analyst in Agricultural Analyses should be absolutely trustworthy, the manufacturers need not fear any injustice being done, or that frivolous criminal proceedings will be instituted against them.

In conclusion, he hoped someone would second the resolution, and that the meeting would be allowed by the Chairman to express a decided opinion on the same.

Discussion,

Mr. W. A. Cox said:—It being a matter of considerable importance to the firm with which I am connected that a uniform method of analysis be adopted in respect to the article in which they are very largely interested, I have called upon the majority of agricultural chemists acting under the Board of Agriculture in the United Kingdom, and found chaotic differences among them regarding method. I therefore propose an amendment to the resolution to the effect that the adoption of official methods of analysis is desirable, provided that the methods adopted are subject to periodical revision.

Mr. F. J. Lloyd seconded Mr. Hughes's resolution, but hoped that it would be enlarged to include all or any official methods of analysis.

J. Hughes' resolution—"That the institution of Official Methods for Agricultural Analysis is undesirable unless subject to periodical revision," was proposed and carried.

In order to unify the methods of analysis to be adopted for testing

resins in oil, the International Congress of Applied Chemistry proposes to establish by the agency of Section I., a statement defining the estimations which should be utilised in ascertaining the purity of the above-mentioned products and the employment of which should be strongly recommended to all analysts.

The Seventh International Congress of Applied Chemistry considers that it is desirable to adopt uniform principles in connection with the application of Reference Tests, and is of opinion that the proposals made by Prof. T. W. Fresenius constitute a suitable basis for these principles.

Sur l'Unification des Méthodes d'Analyse des Essences Résineuses.

By R. Adan, D.Sc., *Belgium*.

Après les dernières discussions qui ont eu lieu à propos de l'analyse des essences de térébenthine, de pin et de résine, on peut dire qu'il est hautement désirable de voir adopter certains chiffres limités dans l'analyse des produits résineux.

Les divergences que l'on trouve dans l'appréciation des essences sont dues pour la majeure partie à la complication des essais et des méthodes suivies dans la recherche des fraudes.

En limitant les méthodes d'investigation aux données les plus constantes obtenues jusqu'à ce jour, il est possible de réaliser une unification des résultats.

Nous examinerons ici le cas des Essences de térébenthine (turpentine—Terpentinöl—Essenza di trementina); Essences de pin (Woodoil—Kienöl—Olio di pino); l'huile de résine (Rosin oil—Harzöl—Olio di resina); l'Essence de résine (Rosin essence—Pinolin—Harz essenz—Harz spiritus—Essenza di resina).

Les diverses fraudes de ces produits peuvent être décelées par les essais suivants:

(1°) *Densité.*—La densité de l'essence de térébenthine pure varie dans d'étroites limites, entre 0·863 et 0·875. Parmi les liquides que l'on mélange à l'essence de térébenthine dans le but de la frauder, les produits légers du pétrole tiennent la première place. Ils ont

tous une densité plus faible que la térébenthine. La densité moyenne des essences de térébenthine oscille autour de 0·8665 à 15° C.

L'essence de pin, est une térébenthine de moindre valeur, retirée par distillation des fragments de racine et de bois des arbres résineux que l'on rectifie ensuite. Ces essences auxquelles il faut joindre les essences de térébenthine colorées en jaune que l'on trouve dans le commerce sous les noms d'essence de Pologne, de Russie, ou d'Hongrie, sont caractérisées par une odeur piquante particulière, dont on ne parvient pas à le débarrasser, et une densité variant entre 0·868 à 0·901.

L'essence de résine est plus lourde que les deux autres, son poids spécifique oscille entre 0·960 et 0·990, c'est un liquide brunâtre ayant une odeur particulière de goudron de bois ou créosote et une réaction fortement acide.

(2°) *Point d'ébullition.*—L'examen d'un grand nombre d'essences de térébenthine permet d'établir que le point d'ébullition de l'essence pure est de 156°5 et que 80 % distillent entre 155° et 165°. La distillation est pratiquement totale à 185°.

L'essence de pin commence le plus souvent à distiller vers 160°. La plus grande partie passe entre 165° et 175°.

La distillation sèche de la colophane donne des liquides oléagineux qui, suivant la température à laquelle ils distillent, prennent des noms différents: les liquides bouillant jusque vers 250° s'appellent essence de résine ou pinoline et ceux bouillant au-delà de 250° s'appellent huile de résine. On extrait de l'essence de résine jaune, une essence vive employée surtout comme succédané de l'essence de térébenthine et de l'huile légère de résine. L'essence vive est constituée par les fractions distillant au-dessous de 170°.

(3°) *Point d'inflammation.*—Le point d'inflammation est caractéristique pour un grand nombre d'essences de térébenthine: il est d'environ 36°. Ce point est très abaissé par la présence d'une faible proportion des produits volatils du pétrole.

L'essence de pin s'enflamme vers 100°; enfin l'essence de résine s'enflamme à 123° environ de l'appareil Pensky, à 155° en vase ouvert.

(4°) *Densité de vapeur.*—La densité de vapeur de l'essence de térébenthine mélangée de produits légers du pétrole, de l'essence de pin

ainsi que de l'essence de résine ne donnent pas d'appréciation certaine.

(5°) *Distillation avec la vapeur d'eau.*—Cette méthode est bonne oxydée en produits acides solubles, tandis que les produits du pétrole (huile de graissage); elle nécessite l'emploi d'appareils compliqués qui tendent à limiter son application.

(6°) *Oxydation par l'acide nitrique.*—C'est peut-être la meilleure méthode quantitative proposée jusqu'ici. En traitant l'échantillon à froid par 10° sous zéro l'essence de térébenthine est graduellement oxydée en produits acides solubles, tandis que les produits du pétrole sont laissés inattaqués. L'essence de résine pure cependant laisse parfois un léger résidu : maximum constaté 2 %.

(7°) *Oxydation par l'acide sulfurique.*—Cette méthode donne de 1 à 2 % de matière insoluble avec l'huile de térébenthine pure. Cette méthode ne peut servir pour l'huile de pin dont elle laisse environ 10 % d'insoluble.

Je propose de l'abandonner comme méthode quantitative de dosage.

(8°) *Pouvoir rotatoire.*—Les diverses sortes d'essence de térébenthine ont sur la lumière polarisée une action bien différente. Tandis que l'essence française est lævogyre, les essences américaines et russes sont dextrogyres. Mais ce pouvoir rotatoire n'est guère constant : il varie entre—31° à—40° pour les essences de France ; + 1 à + 6 pour les essences d'Amérique ; et $a_D = + 9°$ à $+ 16°$ pour les essences de Russie. Etant donné ces divergences, j'estime qu'il vaut mieux ne pas s'appuyer sur cette constante.

(9°) *Indice de réfraction.*—L'essence obtenue par distillation de la térébenthine avec la vapeur d'eau possède un indice de réfraction de 1·466 à 1·473.

L'essence de pin donne pour n_D des valeurs variant de 1·4735 à 1·489.

L'essence de résine possède l'indice n_D le plus élevé : 1·535 à 1·550 à 18°.

Un grand nombre d'autres essais ont été indiqués pour la recherche des fraudes : quelques uns ont de la valeur, mais beaucoup ont un caractère spécieux et ne peuvent être généralisés.

J'ai donc l'honneur de proposer au Congrès le vote de la résolution suivante:

> "En vue d'unifier les méthodes d'analyse et de recherche dans l'essai des essences de produits résineux, le Congrès international de chimie appliquée, émet le vœu de voir s'établir par les soins de la Section I. un tableau définissant les bases à utiliser dans l'estimation de la pureté des susdits produits et dont l'usage serait fortement recommandé à tous les analystes."

This resolution was put to the meeting and carried.

Note upon Marsh and Gutzeit Test.

By H. B. Bishop.

ABSTRACT.

Presence of impurities, such as lead in the zinc, used for the Marsh or Gutzeit test, sometimes causes suspension of hydrogen evolution. Addition of a colloid to the acid solution counteracts this, and facilitates even evolution of hydrogen.

Method for the Determination of Chlorine in the Presence of Hydrochloric Acid.

By C. E. Bolser and J. W. E. Glattfeld, *Dartmouth College, U.S.A.*

In studying the absorption of chlorine by certain organic substances it was desirable to determine the amounts of the reaction product HCl and excess Cl frequently and with reasonable accuracy. No published method could be found to meet the requirements, and the following adaptation of simple titration methods was devised:—

Connect two Geisler absorption bulbs, one of which contains H_2O and the other an approximately normal solution of KI, and force the mixture of HCl and Cl into the bulb containing the H_2O by pressure. Some of the Cl finds its way into the bulb containing KI where it is absorbed. Draw a current of air through the apparatus by means of an aspirator until most of the Cl has been transferred to the bulb containing KI. Transfer the KI and I to a beaker and titrate against decinormal $Na_2S_2O_3$. Transfer the contents of the other bulb to a beaker containing a little KI in solution, titrate the small percentage of I against $Na_2S_2O_3$, then add phenolphthalein and titrate the HCl against semi-normal NaOH. The amounts of Cl and HCl are thus obtained in terms of $Na_2S_2O_3$ and NaOH used.

The semi-normal NaOH is standardized as follows:—A Geisler bulb carrying a $CaCl_2$ tube is filled with H_2O and weighed. HCl, carefully dried, is run in and the apparatus is again weighed. The contents are now transferred to a beaker and the known quantity of HCl is titrated against the solution of NaOH to be standardized. The solution of $Na_2S_2O_3$ is standardized in the same way with the substitution of normal KI for H_2O, $Na_2S_2O_3$ for NaOH, and starch for phenolphthalein.

The method was tested as follows:—Two Geisler bulbs, A and B, were filled respectively with H_2O and normal KI, weighed and connected with a rubber connector. B carried a $CaCl_2$ tube. About a gramme of carefully dried HCl was run in under pressure and the bulbs were again weighed. Cl was then run in and a current of air drawn through the system for about three minutes by means of an aspirator. The bulbs were again weighed. The differences between

the sums of the weights of the two bulbs at successive weighings furnish the data for the amounts of HCl and Cl taken.

The contents of bulb B were transferred to a beaker and titrated against $Na_2S_2O_3$. The contents of bulb A were transferred to a beaker containing a little KI in solution, and the small percentage of I set free was titrated against $Na_2S_2O_3$. Phenolphthalein was then added and the HCl titrated against NaOH. From the sum of the amounts of I in bulbs A and B the chlorine was calculated. After titrating the I from the contents of bulb B it was found that the same amount of NaOH had to be used to obtain the end reaction with phenolphthalein as was required to bring about the same result with an equal amount of H_2O, and it was decided that this bulb contained no HCl.

It is of great importance that in all corresponding titrations equal amounts of liquid be used. The following table shows the results obtained with the weighed amounts of HCl and Cl assumed as accurate in calculating errors:—

HCl by wgt.	Cl by wgt.	HCl by titr.	Cl by titr.	Per cent. error HCl.	Per cent. error Cl.
895·9 mgr.	222·5 mgr.	891·7 mgr.	221·5 mgr.	·47	·45
872·6 "	188·3 "	873·7 "	188·7 "	·13	·21
903·6 "	174·0 "	905·8 "	173·7 "	·24	·17
741·5 "	200·7 "	744·1 "	199·9 "	·35	·40
799·4 "	205·5 "	802·6 "	204·8 "	·40	·34
823·4 "	212·2 "	826·9 "	211·9 "	·43	·14
695·1 "	296·3 "	697·4 "	295·0 "	·33	·44
1112·5 "	215·1 "	1108·0 "	215·9 "	·40	·37

The Examination of China Wood Oil.

E. W. Boughton.

This work was done upon five samples of China wood oil which were received directly from the United States Consul at Hankow, China, and are believed to be a pure unadulterated product, being shipped in sealed bottles which were not opened till they reached the laboratory.

From the dark colour of the samples it was judged that they were hot pressed. We also received a quantity of tung nuts, from which the oil was pressed for us by the V. O. Anderson Company, of Cincinnati. This oil as received was a light clear yellow, differing much in appearance from the other dark turbid samples.

We believe the authenticity of our samples makes the figures obtained worth adding to those of other observers.* Most of the chemical and physical constants fell within the limits of those published.

Serial Number.	Description.			Sp. Gr. at 15·6° C.	Refr. Ind. at 15.6° C.	Sapon. Number.	Acid No.	Ash.	Unsap. Matter.	Total Fatty Acids.
									Per cent.	Per cent.
1	Dark	yellow	Turbid	·9415	1·5204	195·6	0·8	Trace	0·7	93·2
2	,,	,,	,,	·9408	1·5210	195·2	10·2	,,	1·05	93·0
3	,,	,,	,,	·9428	1·5236	194·3	2·0	,,	1·04	94·6
4	,,	,,	,,	·9346	1·5231	190·0	7·2	,,	1·3	94·1
5	,,	,,	,,	·9428	1·5227	193·2	6·6	,,	1·4	94·8
6	Light	,,	Clear	·9421	1·5211	193·1	0·4	,,	1·2	95·0
7	,,	,,	,,	·9423	1·5239	191·4	1·4	,,	0·7	93·7

I have given no iodine value in this table, having found it to be very variable under different conditions. Ordinarily with linseed oil ·2—·3 g. is treated with 30 cc. of Hanus' or Wijs' solution, and let

* L. E. Andes, Drying oils and Boiled oils, page 45.
Sabin, Tech. of Paint and Varnish, page 85.
Lewkowitsch, Lab. Comp. to Fat and Oil Indus., page 42.
Moritz Kitt, Chem. Revue über die Fett- und Harz-Indus., page 241.
Jenkins, Analyst, 1898, page 113.
J. S. C. I., 1897, page 195.
Williams, J. S. C. I., 1898, page 304.

stand one hour on the laboratory table. With tung oil the following figures were obtained:—

Sample Number.	Weight of Oil.	Hanus' Solution.	Time.	Iodine Number.
1	·2002	30 cc.	1 hr.	262·6
1	·3002	"	"	189·2
2	·1998	"	"	257·9
2	·3000	"	"	191·0
3	·1996	"	"	266·0
3	·3002	"	"	180·3

It will be seen that the greater excess of Hanus' solution gives the larger iodine number, and that the results from the same amounts of different oils agree fairly well. This is what would be expected if the ratio of oil to Hanus' solution affects the result.

To discover if a maximum value could be obtained by increasing the amount of Hanus' solution for a small amount of oil, ·05 gram. of oil was treated with 20, 30, 50 and 100 cc. of Hanus' solution, the oil being pipetted out of a chloroform solution containing 2 g. in 100 cc. Bottles allowed to stand one hour at room temperature.

Weight of Oil.	Hanus' Solution.	Iodine Number.
·05	20 cc.	196·5
"	30 "	209·2
"	50 "	202·3
"	100 "	186·4

It will be seen that the maximum seemed to be reached when 30 cc. Hanus' solution was used.

By repeating this, using ·2 g. oil, better checks were obtained, but a maximum was not reached with 100 cc. Hanus' solution, as is shown here:—

Weight of Oil.	Hanus' Solution.	Iodine Number.
·2000	20 cc.	190·6
"	40 "	202·7
"	60 "	210·6
"	80 "	219·3
"	100 "	224·7

A third set, using ·1 g. of oil with different amounts of Hanus' solution, gave the following results:—

Weight of Oil.	Hanus' Solution.	Iodine Number.
·1000	60 cc.	212·5
"	80 "	211·8
"	100 "	206·1

Thus it seems that one part oil to 600 parts Hanus' solution seems to give about the maximum value due to the relative amounts of the two. Hence with this oil we find it is necessary to have present the 70% excess of Hanus' solution that is recommended,* but which is not necessary for linseed.

It was noted that upon different days, other conditions being the same, greatly varying results were obtained, so the effect of temperature was investigated. ·2 g. of oil was allowed to remain in contact with 30 cc. of Hanus' solution for one hour at 10°, 25° and 40° C. The rise in iodine value with the increasing temperature was very marked.

Temp.		Iodine Number.
10°C.	......	158·0
"	......	154·2
25°C.	......	180·6
"	......	174·2
40°C.	......	254·6
"	......	249·0

The poor agreement between duplicates was attributed to variations in temperature which may have amounted to a degree. Another set was run in in which the temperature was regulated to one-fifth of a degree, and a sample of pure raw linseed oil was tested along with the China wood oil. The following are the results:—

Oil.	Weight of Oil.	Hanus' Solution.	Temp.	Iodine Number.
Linseed	·2	25 cc.	15°C.	174·9
"	"	"	"	175·5
"	"	"	20°C.	174·9
"	"	"	"	174·9
"	"	"	25°C.	173·9
"	"	"	"	173·0
"	"	"	30°C.	176·1
"	"	"	"	176·1

* Bur. of Chem. Bul. 81. P. 63.

Oil.	Weight of Oil.	Hanus' Solution.	Temp.	Iodine Number.
China Wood	·2	25 cc.	15°C.	179·3
"	"	"	"	178·6
"	"	"	20°C.	186·3
"	"	"	"	186·9
"	"	"	25°C.	190·8
"	"	"	"	190·1
"	"	"	30°C.	197·2
"	"	"	"	195·9

The iodine value of the linseed oil remained practically constant while that of the tung oil increased with the temperature.

To try the effect of time of contact with the Hanus' solution, two determinations were made standing one hour and two standing 19 hours at room temperature.

Result.

Time.		Iodine Number.
1 hr.	......	177·4
19 "	......	260·1

Another lot of oil was weighed out in ·2 g. portions and subjected to different but less varying times of contact, with the following results:—

Time.	Temp.	Iodine Number.
1 hr.	19·6°C.	186·3
"	"	187·6
2 hrs.	"	190·7
"	"	191·1
3 hrs.	"	192·7
"	"	192·4
4 hrs.	"	193·3
"	"	193·3

25 cc. of Hanus' solution was used. We thus see an increase by lengthening the time of contact.

All of the iodine values quoted for the tung oil in the literature on the subject seem to have been made with the Hübl solution. Two determinations were made by this method:—

Hübl Solution.	Wt. Oil.	Iodine Number.
25 cc.	·1308	177·6
"	·2342	164·0

Four determinations were made, using the same amounts of oil and Hübl solution, two at 19° C. and two at 13°—15° C. The iodine values for the first two were 166·5 and 167·2, and for the second two 167·2 and 168·6. Two more sets were made at temperatures stated in the following table:—

Weight of Oil.	Temp.	Iodine Number.
·2	20–21°C.	159·3
"	"	159·3
"	30–31°C.	158·1
"	"	157·5

Next using different amounts of Hübl solution, as was done with the Hanus' solution, eight determinations were made.

Weight of Oil.	Hübl Solution.	Iodine Number.
·1	20 cc.	162·4
"	30 "	166·7
"	40 "	164·2
"	50 "	166·1

Concentration and temperature seem to have but slight effect when Hübl's solution is used.

Using Wijs' solution in the same way:—

Weight of Oil.	Wijs' Solution.	Iodine Number.
·1	20 cc.	166·1
"	"	164.8
"	30 cc.	172·2
"	"	172·2
"	40 cc.	175·2
"	"	174·6

We see here that the maximum is practically reached at 0·1 g. to 40 cc.

It may be of interest to quote some of the iodine values given for China wood oil:—

Sabin, Tech. of Paint and Varnish	155–165
Andes' Drying Oils and Boiled Oils, &c.	154·6–158·4
Holly & Ladd, Mixed Paints, Colors, Pigments and Varnishes	163
Lewkowitsch, Lab'y Comp. to Fat and Oil Indus. ...	150–165
Kitt, Chem. Revue über die Fett- und Harz-Indus., p. 241...	155–163
Jenkins, Analyst, 1898	149·7–165·7
J.S.C.I., 1897, p. 195	165.7
Williams, J.S.C.I., 1898, p. 305...	155·4–165·6

Conclusions.

1. To obtain a maximum iodine absorption 70% excess Hanus' solution must be present, or a ratio of about ·1 g. to 60 cc. With the Hübl solution ·1 g. to 30 cc. is sufficient.

2. Variations in temperature have a large effect with the Hanus' solution, but practically no effect from a 10° C. variation with the Hübl solution.

3. With Hanus' solution, lengthening the time of action largely affects the results.

4. One is liable, if Hanus' solution be used, to obtain what may seem to be an abnormally high figure for the iodine number, running as high as 260. If Hübl solution be used, however, pure tung oil will give a figure within the limits of published values.

In using McIlhiney's* method for determining the bromine addition and substitution values, I obtained 89·4 (iodine=141·8) add. value as the average of four determinations and 2·8 (iodine equiv. =4·4) substitution value. Using a carbon tetrachloride solution of iodine monobromide, and taking a large excess of the latter, resulted as follows:—

Sabin. Tech. of Paint and Varnish, *p. 47.

Weight of Oil.	Solution.	Temp.	Total Iodine No.	Add. No.	Substitution No.
·15 g.	75 cc.	15°C.	190·4	151·2	39·2
"	"	"	191·5	152·3	39·2
"	"	30°C.	198·1	146·9	51·2
"	"	"	198·1	146·7	51·4

As has been previously stated, the constants other than the iodine value of these samples of China wood oil agreed very well with those published by other observers. There are here appended, however, certain figures, and reactions of this oil, which the author has been unable to find in the literature.

A Livache oxygen absorption test was made, using ·5 g. oil and 5 g. of litharge. The results follow with some figures on linseed oil for comparison:—

Oil Samples.	Per cent. Gain in Weight 24 hours.	Per cent. Gain 48 hours.	Per cent. Gain 96 hours.
China Wood (1)	·11	·99	3·64
" (1)	None	·91	2·84
" (2)	·23	3·37	6·82
" (2)	·33	3·39	8·66
" (3)	·78	4·86	7·56
" (3)	·85	5·82	7·98
Linseed (1)	—	12·90	13·74
" (1)	—	12·87	13·54
" (2)	—	12·77	13·54
" (2)	—	12·94	13·51

It will be seen from this that for 96 hours the oxygen absorption is much less than for linseed.

Upon heating one hour in an air oven at 105° C. in a shallow dish, a skin formed on the surface of the oil and the gain in weight varied from 0·22 to 0·75%.

The Liebermann-Storch* rosin test when made with the alcoholic extract of tung oil gave a claret colour which was not the violet of colophony, but resembled the colour given by Dammar gum.

The Stannic-Bromide† rosin test gave a violet colour which might be mistaken for rosin.

* J. S. C. I., 1888, pp. 135–136.

† Allen, Com. Org. Anal., 11, 463.

When a solution of iodine in some such solvent as chloroform or carbon bisulphide is added to tung oil a dark jelly results.* Mixtures of linseed and tung oil in different proportions were made and this test applied. Result:—

Composition of Mixture—

Linseed 50 % ... ... / Tung 50 %...	Solidifies immediately.
Linseed 80 % ... ... / Tung 20 %...	Solidifies immediately.
Linseed 90 % ... ... / Tung 10 %...	No solidification in 48 hours.
Linseed 95 % ... ... / Tung 5 %	No solidification in 48 hours.

By slightly modifying this procedure 10% of tung oil may be detected. An equal volume of chloroform solution of iodine is added to the oil in a large size test tube and heated on the steam bath till the chloroform is driven off. The tube is then heated one hour in an oil bath at 200° C. This will solidify a mixture of 90% linseed and 10% tung oil, while straight linseed remains liquid.

Another test which will identify 10% of tung oil in a mixture of the two is as follows: In a glass stoppered tube place about 10 c.c. of the oil and 10 c.c. strong nitric acid. Shake well and place in ice water. On standing the oily layer will solidify if 10% tung oil be present.

The considerable difference in the refractive indices of linseed and tung oil makes easy the approximate estimation of them in a mixture as is shown here:—

Composition.	Refr. Index 15·6°C.	(Calculated.)
Tung oil	1·5238	—
Tung oil 5 % ... ... / Linseed oil 95 %	1·4866	1·4862
Tung oil 10 % ... ... / Linseed oil 90 %	1·4882	1·4882
Tung oil 20 % ... ... / Linseed oil 80 %	1·4922	1·4921
Tung oil 50 % ... ... / Linseed oil 50 %	1·5037	1·5040
Linseed	1·4842	—

These tests and results are preliminary to the detection of varying amounts of China wood oil in varnish, which I hope to work upon in the near future.

My thanks are due to Mr. Percy H. Walker for directing this work.

* Lewkowitsch, Oils, Fats and Waxes.

Méthode d'analyse des Huiles essentielles contenant des Alcools Terpéniques tertiaires.

Par VICTOR BOULEZ.

LE dosage des alcools, principe si important, dans les essences, se fait couramment par l'éthérification à l'anhydride acétique. Mais chacun sait que les alcools tertiaires ne se laissent pas éthérifier facilement; c'est à cause de cela que deux des principaux alcools des huiles essentielles : le linalol et le terpinéol, n'ont pu être dosés jusqu'à présent. C'est la lacune que ma méthode est venue combler en partant d'un principe susceptible de généralisation : la dilution de l'alcool à éthérifier dans un solvant neutre ou indifférent. J'ai démontré dans mes communications préliminaires, parues dans le bulletin de la Société chimique de France, qu'il est nécessaire que la dilution soit faite dans un milieu indifférent. Depuis ces notes j'ai modifié ma méthode et c'est ainsi améliorée que je la présente en extrait ici.

TABLEAU D'ANALYSES COMPARATIVES D'ESSENCES DIVERSES PAR LA MÉTHODE COURANTE ET LA MÉTHODE BOULEZ.

Nature des essences.	Méthode courante.		Méthode Boulez.	
	Éthers.	Alcool libre.	Éthers.	Alcool libre.
	%	%	%	%
1. Linaloë	8·80	48·08	8·80	81·04
2. Linaloë	6·20	40·00	6·20	76·10
3. Cèdre	7·65	8·51	7·65	35·41
4. Patchouly	7·45	21·60	7·45	48·88
5. Petit grain Paraguay ..	31·35	28·06	31·35	45·16
6. Géranium d'Afrique ..	16·97	57·44	16·97	80·47
7. Géranium d'Afrique ..	18·60	51·93	18·60	67·23
8. Kuro-Moji	11·27	29·17	11·27	40·59
9. Lavande suspecte	34·23	27·70	34·23	39·71
10. Lavande	25·82	25·43	25·82	59·01
11. Lavande	31·52	23·05	31·52	51·07

Pour rendre évidente la supériorité de ma méthode voici en un tableau comparatif des résultats obtenus par la méthode courante et par ma méthode appliquées à diverses huiles essentielles, qui prouvent aussi que par ma méthode on arrive encore à pénétrer plus avant

dans la composition des essences, en faisant ressortir l'existence de principes alcooliques qui avaient échappé à la détermination jusqu'à ce moment.

Ces chiffres sont probants et démontrent que dans tous les cas, ma méthode donne des résultats intéressants. Sans les discuter, ce qui allongerait ce résumé, il est nécessaire de faire remarquer que, notamment pour les essences de linaloë, dont l'analyse est impossible jusqu'à présent, et pour les essences de lavande, que l'on arrive à falsifier très habilement, ma méthode permettra de reconnaître les essences suspectes.

Pour effectuer l'analyse de ces essences par ma méthode, on opère d'abord le dosage des éthers comme d'ordinaire et l'on détermine ensuite les alcools de la manière suivante :

Je pèse dans un ballon de 250 c.c. un gramme environ de l'essence à examiner et 25 c.c. de méta-xylène (poids 22 gr. environ), on y ajoute 40 gr. anhydride acétique, 3 gr. acétate de sodium fondu, et l'on fait bouillir environ neuf heures. On vérifie le poids du flacon avant et après la cuisson pour s'assurer qu'il n'y a pas eu de pertes. On laisse refroidir, additionne d'environ 50 gr. d'eau distillée, chauffe une demi-heure au bain-marie, sépare l'eau à l'entonnoir à décantation, fait *un seul lavage* à l'eau distillée chaude, recueille le mélange essence-xylène dans un flacon sec, met du sulfate de soude anhydre et après refroidissement filtre. Sur 5 gr. environ du filtrat et après neutralisation exacte de l'acidité libre, on fait écouler 25 c.c. de soude alcoolique titrée et après saponification on titre comme d'habitude les éthers formés. Il faut rarement prolonger la durée de l'ébullition ; quelquefois il n'est pas nécessaire de faire cuire aussi longtemps. Outre le linalol et le terpinéol j'ai pu encore acétyler intégralement la terpine, qui fonctionne bien comme un alcool di-atomique.

Les modifications que j'ai fait subir à ma méthode sont : dilution plus grande dans le solvant neutre de l'essence à éthérifier (donc moins d'essence à employer, ce qui n'est pas à dédaigner) ; suppression du lavage au carbonate de soude et réduction à un seul lavage à l'eau pure des lavages successifs habituels. On sait à quelles manipulations et réactions compliquées on doit avoir recours pour obtenir les éthers des alcools tertiaires ou autres qui sont détruits par l'éthérification ; ma méthode pourrait encore trouver une application plus générale pour la préparation de ces éthers.

The Analysis of Shellac.

By PARKER C. McILHINEY, Ph.D., 7 *East 42nd Street, New York.*

ABSTRACT.

The analytical examination of shellac to determine its purity has become in the last few years a matter of increasing importance. The most important adulterant is common rosin or colophony. The methods which have been employed to detect and determine this adulterant have been a determination of the acidity of the sample which has not been found satisfactory, the determination of the iodine figure first by the old Hubl process and later by the improved Wijs-Langmuir process. The Wijs-Langmuir process is the one in most common use at the present time in the United States and gives results that are very satisfactory within known limitations. The principal objection to it is that it is an indirect method. The author describes the details of procedure of a method of analysis in which the rosin is actually separated from the shellac so that it may be weighed, examined, and exhibited. The method consists of the following steps:—

1. Solution by gentle heat of 2 grams of the shellac in 20 c.c. of absolute alcohol.
2. The addition with agitation of 100 c.c. of petrolic ether.
3. The addition with agitation of 100 c.c. of water.
4. The thorough agitation of the separated petrolic ether with the aqueous diluted alcohol and its separation from the latter in a tapped separator.
5. Washing the petrolic ether with a little water.
6. Filtering the petrolic ether solution into a dry separator.
7. The addition to the petrolic ether solution of 25 c.c. of standardised approximately N/5 NaOH in 50 per cent. alcohol and the agitation of the two together followed by their separation on standing.
8. Drawing off into a tared flat-bottomed vessel the aqueous alkaline layer.
9. Washing the petrolic ether with a little 50 per cent. alcohol and addition of the washings to the alkaline solution in the dish.
10. Neutralisation of the whole of the soda in the alkaline liquid by the appropriate volume of standard hydrochloric acid.
11. Evaporation of the neutralised alkaline solution to dry-

ness, weighing and subtracting the weight of the NaCl as determined by a separate experiment on the N/5 soda solution.

Results are quoted showing that the lower pure grades of shellac give approximately 1·5 per cent. of extract which requires about 7/10 c.c. of N/10 alkali to neutralise that produced from one gram of shellac. The higher grades of shellac may give up to 2·5 per cent. of extract.

Rosin is stated to give approximately 85 per cent. of its weight, and the calculation is made by the formula:

$$\frac{\%\text{ extract found minus }2\%}{85\text{ minus }2} = \%\text{ resin present.}$$

Ueber eine quantitative Bestimmung der Fettsäuren in Fetten, Oelen und Seifen.

Dr. Karl Braun, *Berlin.*

Die direkten Methoden der quantitativen Bestimmung der Fettsäuren versagen fast alle. Mit Hülfe indirekter Methoden dagegen lassen sich, wie z. B. aus der Verseifungszahl die % Fettsäuren berechnen.

In ähnlicher Weise kann man die Fettsäuren derart bestimmen, dass man das fettsaure Kalium oder Natrium in geeigneter Weise in die Silbersalze überführt und aus der Menge des gebundenen Silbers die Fettsäuren berechnet.

Determination of Sulphur Dioxide in Dry Gases.

By T. Lynton Briggs.

ABSTRACT.

Orsat apparatus made available for the purpose by use of chromic acid in concentrated phosphoric or sulphuric acid solution.

Prof. Philip Browning read a

Report of Work in Analytical Chemistry in American Universities and Colleges during 1906-08.

An Abstract of the Methods of the United States Steel Corporation for Commercial Sampling and Analysis of Iron Ores.

By J. M. Camp.

Iron Ore Sampling in General.

A brief introduction upon iron ore sampling emphasizing the latitude necessary under different conditions is given.

Car Sampling at Producer's End.

Samples are taken uniformly over the surface of the cars on parallel lines or over a zigzag course. Very lumpy ore is sampled by the rope net system. The proper proportion between lump and fine ore is maintained, and a portion of the ore is reserved in a closed can for the moisture determination.

Cargo Sampling at Consumer's End.

Several practices are followed, depending upon the conditions.

Samples may be taken from each grab during the unloading. The general plan is to sample the tops of the piles before unloading has commenced, then the exposed faces of ore during the process of unloading, or after the greater part of the ore has been removed.

Car Sampling at Consumer's End.

Not less than ten and as many as fifty equal sized samples are taken from each car at points symmetrically arranged on the piles of ore in each end of the car. The proper proportion of lump and fine ore is maintained, and a portion of the sample is reserved for the moisture determination.

Preparation of Samples in General.

The ideal practice of preparing samples is outlined.

Preparation of Sample at Producer's End.

The sample is dried, and alternately crushed and quartered until about three ounces remain. This amount is crushed until it will all pass through a hundred mesh sieve, and constitutes the sample for analysis.

Preparation of Sample at Consumer's End.

The practice is essentially the same as previously outlined.

METHODS OF ANALYSIS.

Iron.

One-half to one gram of the sample is dissolved in hydrochloric acid and stannous chloride. The determination is completed by the bichromate or the permanganate titration. The residue, if suspected of containing iron, is fused with sodium carbonate, the fusion is acidified and the iron titrated.

Silica.

Hydrofluoric Acid Method.

One gram of the sample is dissolved in hydrochloric acid and the solution evaporated to dryness. The residue is dissolved in dilute hydrochloric acid and hot water, the insoluble matter is filtered off, ignited, and weighed. The residue is treated with sulphuric and hydrofluoric acids, the silica being determined by difference.

Using one to five grams when all or part of the Filtrate is used for the Phosphorus or other determinations.

One to five grams of the sample are dissolved in hydrochloric acid, the solution is filtered and the filtrate evaporated to dryness. The insoluble residue is fused with sodium carbonate, the fusion is acidified with hydrochloric acid and evaporated to dryness. The residue containing the greater part of the iron is dissolved in hydrochloric acid, and if the solution is to be used for the phosphorus determination, the excess acid is evaporated and nitric acid added. The residue from the fusion is moistened with dilute hydrochloric acid, and dissolved in hot water. Both solutions are filtered into a suitable flask if the phosphorus determination follows, otherwise into a volumetric flask. The residue is ignited and weighed as silica.

Phosphorus.

Fusion Method.

The entire filtrate obtained in the preceding determination, or an aliquot part of the filtrate in the volumetric flask, after being boiled with nitric acid is rendered ammoniacal, and nitric acid is added with from 5 to 10 c.c. in excess. To the solution heated to 80° C. ammonium molybdate solution is added, the flask is agitated and the precipitate allowed to subside. The determination may be completed gravimetrically: by direct weighing of the yellow precipitate on a tared filter after drying at 110-120° C.; or by dissolv-

ing this precipitate with ammonium citrate solution, reprecipitating with magnesia mixture and estimating as magnesium pyrophosphate. The estimation may be effected volumetrically: with titration of the yellow precipitate by the acid alkali method; or after solution in ammonia and reduction with zinc by the permanganate titration.

Direct Determination of the Soluble Phosphorus.

One to five grams of the sample are dissolved in hydrochloric acid, the excess acid is evaporated and the solution is filtered into a suitable flask. Ammonia and nitric acid are added, as previously described, and the determination is completed by one of the methods already given.

By Ignition of the Insoluble Residue.

One to five grams of the sample are dissolved in hydrochloric acid and the solution is filtered. The insoluble residue is ignited and transferred to the filtrate, which is evaporated to dryness. The residue is dissolved in hydrochloric acid, the excess evaporated, and nitric acid is added. The solution is filtered into a suitable flask and the determination completed as previously described. With unknown ores, and at regular intervals with all ores, as a check, the insoluble residue is fused as outlined under the Fusion Method.

When Titanium is Present.

Two grams of the sample are fused with sodium carbonate, the fusion is disintegrated with hot water and the residue filtered off. The filtrate is acidified with hydrochloric acid and evaporated to dryness. The residue is moistened with dilute hydrochloric acid, dissolved in hot water, the solution is filtered, and the determination is completed in the usual manner. The phosphorus may be separated from the large amount of sodium chloride present in the filtrate by precipitation with a ferric iron solution and ammonia. The resulting precipitate is filtered off, redissolved in nitric acid, and the determination is completed as previously directed.

Alumina.

Phosphate Method.

For this determination the hydrochloric acid filtrate from the silica, representing one gram of the sample, or the hydrochloric acid solution of the precipitated iron and alumina in the gravimetric estimation of manganese is used. To the cool, dilute solu-

tion, a solution of ammonium phosphate is added, then ammonia until a faint precipitate persists. This is dissolved with $1\frac{1}{2}$ c.c. of strong hydrochloric acid, and a solution of sodium hyposulphite is added. The solution is heated to boiling, ammonium acetate and acetic acid are added, and boiling is continued ten minutes. The precipitate is filtered off, ignited, and weighed as aluminium phosphate.

Ether Method.

One to five grams of the ore are dissolved in hydrochloric acid the solution is filtered and evaporated to dryness. The residue is subjected to hydrofluoric acid treatment; it is then fused with potassium bisulphate, the fusion is dissolved in hydrochloric acid, and the solution evaporated to dryness. The residue containing the greater portion of the iron is dissolved in hydrochloric acid, S. G. 1·13, the solution is transferred to a separatory funnel and an ether extraction made. The acid solution is drawn off and combined with the dissolution obtained by dissolving the residue from the fusion. The ether is evaporated, and any ferrous iron present oxidized. A basic acetate precipitation is made, followed by an ammonia precipitation, the second precipitate being ignited and weighed as oxides of iron, alumina, and phosphorus. The iron is determined by fusion with sodium carbonate and solution in hydrochloric acid, or by direct solution in hydrochloric acid and stannous chloride, with subsequent titration. The weight of the combined oxides minus that of the ferric oxide and phosphorus pentoxide gives the weight of alumina.

Manganese.

Gravimetric Method.

The solution, representing one gram of the sample, after fusion of the insoluble residue and separation of the silica, is boiled with nitric acid. A basic acetate separation is then made, if more than 1 per cent. manganese is present, two separations are effected. The filtrate, or the combined filtrates are heated to boiling, and the manganese is precipitated by the addition of ammonia and ammonium persulphate. After ten minutes boiling, the precipitate is filtered off, ignited, and weighed as manganese tetroxide, or it may be dissolved, reprecipitated, and estimated as manganese pyrophosphate. The ignited precipitate of magnanese tetroxide is liable to be contaminated with small amounts of silica, which may be determined and deducted from the original weight.

Volhard's Method.

One or two grams of the sample are dissolved in hydrochloric acid. Nitric acid or potassium chlorate is added, and the excess acid evaporated. The solution is diluted, transferred to a volumetric flask, and zinc oxide emulsion is added. An aliquot part of the solution is taken, heated to boiling, and titrated with permanganate. Or the titration is effected in the entire solution in the presence of the iron precipitate.

Colour Comparison or Titration Method.

One gram of the sample is dissolved in hydrochloric and sulphuric acids, and evaporation is conducted until sulphuric acid fumes appear. The solution is transferred to a small volumetric flask, and an aliquot portion is transferred into a test tube if for colour comparison, or into a small flask if for titration. The solution is heated, and the manganese oxidized by silver nitrate and ammonium persulphate. The manganese is estimated by comparison of the permanganic acid colour against a standard, or by titration with sodium arsenite. If the insoluble residue is suspected of containing manganese, it is filtered off and decomposed with hydrofluoric and sulphuric acid treatment.

Peroxide Reduction Method.

One-half to three grams of the sample are dissolved in hydrochloric acid, the residue being subjected to hydrofluoric acid treatment if suspected of containing manganese. The solution is evaporated almost to dryness, nitric acid is added, the solution boiled until clear, and the manganese is precipitated with potassium chlorate. The solution is cooled, diluted, and a definite amount of hydrogen peroxide is added. After reduction, the excess peroxide is determined by permanganate titration, the relative value between these solutions being known.

Lime.

The filtrate from the persulphate precipitation of the manganese, after the basic acetate or ammonia separation of the iron and alumina, is used for this determination. After the addition of ammonium oxalate and ammonia, the solution is evaporated to a volume of 150 c.c. Ammonia is again added, the solution is boiled, the precipitate is filtered off, ignited, and weighed as lime. The ignited precipitate is liable to be contaminated with small amounts of silica, which may be determined and deducted from the original weight.

The precipitate may be dissolved on the filter in dilute sulphuric acid, and the lime determined by permanganate titration.

Magnesia.

The filtrate from the calcium oxalate is made slightly acid with hydrochloric acid and a solution of ammonium phosphate is added. The solution is cooled, then 25 c.c. of ammonia are slowly added. After continuous stirring for one hour, or after sufficient time on standing for complete precipitation, the precipitate is filtered off, ignited, and weighed as magnesium pyrophosphate.

Sulphur.

Fusion Method.

One gram of the sample is fused with sodium carbonate and a little potassium nitrate. The fusion is disintegrated in hot water and the solution filtered. To the filtrate a slight excess of hydrochloric acid is added, the solution is heated to boiling, and the sulphur precipitated with barium chloride. The precipitate is allowed to subside, is filtered off, ignited, and weighed as barium sulphate. If the ignited precipitate is suspected of containing traces of silica, it may be purified by the addition of a drop of sulphuric and a few c.c. of hydrofluoric acids.

Wet Method.

Five to ten grams of the sample are dissolved in aqua regia, and the solution is evaporated to dryness. The residue is dissolved in hydrochloric acid and the excess acid evaporated. The solution is filtered, the filtrate is heated nearly to boiling and barium chloride added. The excess acid is again evaporated, the solution is diluted, the precipitate allowed to subside and the determination is concluded as previously described.

Ignition Loss.

One gram of the sample is ignited in a crucible with a closely fitting cover until constant weight is obtained.

Moisture.

Not less than two kilograms of the sample reserved for the moisture determination is dried at 100° C. until constant weight is obtained.

Rapid Analysis of Babbitt Metal.

By Percy H. Walker and H. A. Whitman.
Bureau of Chemistry, Washington, D.C., U.S.A.

Methods for the analysis of alloys of lead, tin, antimony and copper which are based upon the separation of lead and copper from antimony and tin by the use of alkaline sulphide solutions are all exceedingly tedious, though with the necessary care, skill and patience, it must be admitted that a method based upon this principle gives results of greater accuracy than any of the more rapid methods. This method is, however, so tedious that it can seldom be used in a commercial laboratory, and when it is used the chances of loss are so great that frequently the whole analysis must be recommenced after spending several days on the tedious separation.

The more rapid methods which are often based upon the separation of antimony and tin by treatment of the alloy with nitric acid are open to the serious objection that one portion of the alloy is used for several determinations and the errors in separation appear again in the determination of the individual metals.

It is highly desirable that we have a method using a separate portion of the alloy for each determination, and that the metal to be determined in each case be dissolved before it is determined. Except for the method of separating copper (and even here Fresenius (Quantitative Analysis, Vol 1, p. 684) gives a similar method of separating copper from nickel), there is no new method suggested in the scheme we present. The details of the various determinations have, however, been studied and sources of error in the determination of lead and copper are pointed out, so that by following the method as described and applying the proper correction, as accurate results can be obtained as by the alkaline sulphide process in a far shorter time and with much less labour.

The Method.

Copper.—Weigh 1 gram of the alloy into a 250 c,c. beaker, add 20 c.c. hydrochloric acid and 5 c.c. water, heat and complete solution by adding nitric acid in small amounts. With most alloys solution can be effected in a very few minutes and without adding more than

one or two c.c. of nitric acid. Evaporate off the acid on steam bath. It is not necessary to carry to complete dryness, but practically all the acid should be driven off and the residue should be pasty. Add 25 c.c. of a solution made of 200 grams tartaric acid, and 260 grams potassium hydroxide, the whole being made up to 500 c.c. with water. Heat on the steam bath until solution is completed, add 25 c.c. water, boil, add 25 c.c. of a 0·2 per cent. invert sugar solution, boil for two minutes, filter through asbestos, wash the precipitate of Cu_2O with water, dissolve in nitric acid, catching the copper solution in a 200 c.c. flask, and determine copper by any good volumetric method. We have found that equally good results can be obtained by following Low's Iodide Method (J. A. C. S. 24, 1082, 1902), or by Jamieson, Levy and Wells' Thiocyanate and Iodate Method (J. A. C. S. 30, 760, 1908). The results are uniformly a little low. This error is not due to volumetric methods employed, both of which give exceedingly accurate results; but nearly 6 per cent of the copper present is not precipitated as Cu_2O. This loss is uniform, for if we add 6 per cent. of the copper determined, the result will be the per cent. of copper in the alloy.

The statement is frequently made that if a babbitt metal is decomposed by nitric acid, evaporated to dryness, taken up with nitric acid and filtered, that copper can be determined in the filtrate with an error of not more than one or two tenths of one per cent. This is not the case: the error with an alloy containing 5 per cent. of copper will frequently be from ·5 to ·7 per cent., while by the method described above without correction the error will be less than ·3 per cent., and by applying the correction this error is removed entirely.

Lead.—Dissolve 0·5 to 1 gram alloy in a 250 c.c. beaker as in the determination of copper, when solution is complete, evaporate to dryness on the steam bath, add 5 c.c. strong hydrochloric acid (with as much as 10 per cent. Sb use 10 c.c. HCl), warm for a few minutes, remove from steam table, add, with stirring, 150 c.c. 95 per cent. alcohol, let stand at room temperature for two hours, filter on a Gooch crucible, wash with 95 per cent. alcohol, using about 100 c.c. Suck as dry as possible, dry crucible in an air bath (one hour at 105° C. is sufficient, though the lead chloride can be heated at 150° with perfect safety). Weigh as $PbCl_2$, add ·0085 gram to the weight of the precipitate and multiply by ·74478, the product gives the weight of lead.

The method of separating lead as chloride has been used by several authorities. G. W. Thompson* (Stillman—"Engineering Chemistry," 3rd ed., p. 401) separates as chloride and then determines as chromate. Olsen ("Quantitative Analysis," p. 136) separates and weighs as chloride. Neither of these authors, however, gives methods which can give correct results, for the solubility of lead chloride in mixtures of alcohol and hydrochloric acid seems to have been overlooked by both. This may cause errors of several per cent. if the conditions are not made uniform and allowance made for the lead chloride dissolved. The amount of acid present is also of importance. If a large amount of hydrochloric acid is present the liquid will dissolve more lead chloride; if too little acid is present there is danger of precipitating oxychlorides of antimony or tin. We have found, however, that the above proportions of acid and alcohol will cause no precipitation of metals other than lead and will dissolve an amount of lead equal to the correction applied. This holds true for alloys high in lead and for alloys high in tin.

Antimony is best determined by W. H. Low's method (J. A. C. S. 29, 66), which we have slightly modified as follows: To 1 gram alloy in a 450 c.c. Erlenmeyer flask, add 10 to 15 c.c. strong sulphuric acid, heat on hot plate until alloy is thoroughly decomposed. This is generally accomplished in about 30 minutes from the time fumes of SO_3 begin to be given off. Cool, add 200 c.c. water and 20 c.c. strong hydrochloric acid, boil to make sure that all SO_2 is driven off, cool and titrate rapidly with potassium permanganate which has been standardised against metallic antimony. The true end point is when a pink colour shows after agitating the liquid, though this pink will very soon disappear. The only change we make in the Low method of procedure is to add somewhat less hydrochloric acid. The results are sufficiently accurate for commercial purposes, but the tendency is to get results ·3 to ·4 per cent. high.

Tin is also worked by W. H. Low's method, except that we have

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* In Thompson's original article which was published in J. Soc. Chem. Ind. 15 : 179-182, 1896, he states that by using as he does potassium chloride along with hydrochloric acid the amount of lead left in after precipitating as chloride with alcohol amounted only to 0·3 per cent. when he was working with solder, and in a private communication since this was written, Dr. Thompson tells us that he makes an allowance for the lead chloride dissolved. He, however, weighs his lead as chromate.

found it more satisfactory to use a separate portion of the alloy and reduce with steel turnings instead of with metallic antimony. Treat from ·2 to 1 gram of alloy (do not use an amount of alloy containing more than ·2 gram tin) in a 450 c.c. Erlenmeyer flask with 10 to 15 c.c. strong sulphuric acid, heat on the hot plate until the alloy is thoroughly decomposed, cool, add 200 c.c. water, 30 c.c. strong hydrochloric acid, and about 1 gram of steel turnings, heat and when reduction appears complete, but before the last particles of steel have dissolved, place a two-hole rubber stopper in the neck of the Erlenmeyer flask—one hole of the stopper should carry a tube reaching below the surface of the liquid, the other hole should carry the short arm of a bent tube, the long arm of which reaches nearly to the bottom of a 100 c.c. Erlenmeyer flask containing a solution of sodium bicarbonate, this small Erlenmeyer is held on the bent tube by a cork which has a notch cut in it to act as a vent. Through the tube reaching below the surface of the liquid in the large Erlenmeyer pass a current of carbon dioxide, heat to boiling until all steel is dissolved, continue passing CO_2 and cool as quickly as possible; loosen stopper, but let current of CO_2 continue, add cautiously some starch solution and titrate with N/10 iodine. It is necessary to absolutely exclude air and to standardise the iodine solution with pure tin. Results are accurate.

To test the copper method, amounts of copper, tin, antimony, and lead were weighed out in the proportions of about 4 copper, 13 lead, 8 antimony, and 75 tin, the copper being weighed accurately each time and the copper determined in the mixture as described. The following results being obtained:—

Weight of mixed metal.	Copper taken.	Copper by titration.	Copper calculated by taking 106 per cent. of copper by titration.
Grams.	Grams.	Grams.	Grams.
1	·0446	·0417	·0442
1	·0446	·0422	·0447
1	·0446	·0418	·0443
2	·0863	·0799	·0847
2	·0849	·0803	·0851
1	·0407	·0376	·0399
1	·0407	·0382	·0405

An alloy, No. 4873, containing 4·66 per cent. copper was then taken and the following results obtained:—

Weight of alloy taken.	Per cent. copper by titration.	Per cent. copper by taking 106 per cent. of copper by titration.
Grams.		
2	4·35	4·61
2	4·34	4·60
2	4·49	4·75
2	4·42	4·68
2	4·43	4·69
1	4·40	4·66
1	4·37	4·63
1	4·35	4·61
2	4·43	4·70
2	4·39	4·65

Average by proposed method, 4·66. Alloy No. 4,873 had been previously analyzed by the alkaline sulphide method with the following results on copper:—4·60, 4·98, 4·37, and 4·68, giving an average of 4·66, the same as by the proposed method. Not only are the determinations carried out by our method much more rapidly than by the alkaline sulphide method, but the individual determinations agree better among themselves.

To test the lead method a similar method was followed, the metals being taken in about the same proportion as for testing the copper determination. Varying amounts of strong hydrochloric acid were used, and the following results obtained:—

(A) Weight of mixed metals.	(B) Weight of lead.	(C) Hydrochloric acid used.	(D) Weight $PbCl_2$ found.	(E) Weight of $PbCl_2$ + ·0085 g.	(F) Per cent. Pb from (E).
Grams.	Grams.	C.C.	Grams.	Grams.	
2	·2865	10	·3649	·3734	13·60
2	·2819	10	·3603	·3688	13·73
1	·1418	5	·1978	·2063	15·36
1	·1416	15	·1818	·1903	14·17
1	·1472	25	·1777	·1862	13·87
1	·1489	10	·1917	·2002	14·91

These results indicate that better results are obtained when using

1 gram of alloy than when using 2 grams, and also indicate that as much as 15 c.c. of strong hydrochloric acid could be used without changing the results materially.

The method was then used in determining lead in two alloys with the following results:—

Alloy.	(A) Weight of alloy taken.	(B) Hydrochloric acid used.	(C) Weight of $PbCl_2$ found.	(D) Weight of $PbCl_2$ + ·0085 g.	(E) Per cent. lead from (D).	
	Grams.	C.C.	Grams.	Grams.		
4874	1	5	·9924	1·0009	74·57	
4874	1	5	·9940	1·0025	74·69	
4874	1	10	·9833	·9918	73·81	
4874	1	10	·9857	·9942	74·07	
4874	1	15	·9815	·9900	73·73	
4874	1	15	·9800	·9885	73·63	
4873	1	5	·1683	·1768	13·17	$PbCl_2$ stood 18 hours before filtering.
4873	1	5	·1676	·1761	13·12	
4873	1	5	·1661	·1746	13·01	$PbCl_2$ stood 1 hour before filtering.
4873	1	5	·1636	·1721	12·81	
4873	1	3	·1706	·1791	13·34	$PbCl_2$ stood 2 minutes before filtering.
4873	1	2	·1689	·1774	13·22	
4873	1	1	·1705	·1790	13·33	

The two alloys used had been carefully analyzed by the alkaline sulphide method, with a final weighing of lead as sulphate.

No. 4,874 gave 74·13 per cent., 74·71 per cent., and 74·44 per cent. lead, averaging 74·43 per cent. lead.

No. 4,873 gave 13·34 per cent., 13·28 per cent., 13·07 per cent., and 13·33 per cent. lead, averaging 13·26 per cent. lead.

On alloy 4,874 the results obtained by the chloride method, using 15 c.c. hydrochloric acid are somewhat low, and as 10 c.c. is enough it is best to use this amount. The last three determinations on alloy 4,873 indicate that accurate results can be obtained by using even less than 5 c.c. acid and filtering at once.

The methods for tin and antimony are in all essential respects well-known methods, but we have found in the laboratory that they yield good results as the following indicate:—

Alloy.	Antimony by alkaline sulphide method, with final weighing as Sb_2S_3.		Antimony volumetric.	Tin by alkaline sulphide method, with final weighing as SnO_2.	Tin-volumetric.	
4874	17·28 17·33 17·53 17·68	17·46	17·76 17·90	7·82 8·10	7·98 7·92	
4873	8·02 7·91 8·28 7·91	8·03	8·45 8·38	73·98 74·03	73·87 75·47 74·33 74·42 73·51 74·98 73·51	74·16

We wish to express our thanks to Mr. F. W. Smither who made the analyses of the two samples of babbitt metal by the alkaline sulphide method. He used the method described in N. W. Lord's "Notes on Metallurgical Analyses," 2nd Ed. Also to Dr. H. C. McNeil for suggestions on the various methods tried.

On Jaffé's colorimetric method for the estimation of Creatinine.

By A. Chaston Chapman.

The author has shown that the red colouration on which this method is based depends, not on the formation of creatinine picrate, but is due to the reduction of the picric acid in alkaline solution to a mixture of amino-dinitro phenol (picramic acid) and diamina-nitro phenol, the alkaline salts of which are deeply coloured. The same colouration is produced by numerous reducing agents, such as nascent hydrogen, hydroxylamine, acetone, aldehyde, ammonium sulphide, and titanium trichloride. Creatinine acts as a powerful reducing agent, and if it is present in excess the picric acid may undergo reduction to colourless triamino-phenol. Colour measurements showed the red colouration to be due to both the monamino and the diamino phenol, and that solutions of the sodium salt of

picramic acid could not be used for matching purposes. Since the colouration is due to a somewhat complex reducing action, it is clear that the conditions under which the test is carried out must be fairly closely defined if accurate results are to be obtained.

Influence of temperature.—This factor is of considerable importance, since up to a certain point the colour is increased, after which there is a reduction due to the formation of triamino-phenol.

Influence of time.—This factor is of much less importance than the preceding, and slight differences have no appreciable influence on the results. The general effect is, however, of the same character as in the case of the temperature factor—that is to say, there is at first an increase and then a reduction of the colour intensity.

Influence of the presence of dextrose.—As in certain commercial products, dextrose and creatinine may occur together, experiments were made to ascertain whether the former substance exerted any influence on the estimation of the latter. It was found that in the cold, and under the ordinary conditions of the test, dextrose was without appreciable effect.

In conclusion, attention is called to the necessity of working in sufficiently dilute solutions, in analysing highly coloured products, since the disturbing effect of the colour may be very considerable.

Discussion.

Sir T. E. Thorpe asked if Mr. Chapman had attempted to ascertain what substances were formed on the oxidation of the creatinine.

Dr. Wiley remarked that the Jaffé reaction was one of considerable importance, not only in connection with the analysis of certain commercial products, but also in relation to problems of metabolism. Colour reactions were very delicate, but were sometimes apt to be uncertain, and it was well that the method should have been worked out as it had been by Mr. Chapman. The results were very interesting.

Mr. Chapman replied that it was a little difficult to understand why creatinine should function as such a powerful reducing agent. He had made numerous experiments on the point, but had not succeeded in isolating any definite products. The CO group was, of course, oxidised to CO_2.

Factors which influence the Kreatinin Determination.*

F. C. Cook.

From the Laboratory of Animal Physiology, Bureau of Chemistry, United States Department of Agriculture.

The conclusions drawn from this work are briefly, viz.:—

In determining kreatin or kreatinin alone or in meat extracts it is advisable to add 30 cc. of 1·2 per cent. picric acid solution.

Using commercial samples of kreatin and kreatinin 15 cc. of 10 per cent. NaOH gave lower results than when 5 or 10 cc. were present. With a meat extract 5 cc. gave low results; 10 cc. and 15 cc. gave practically identical values.

Dilution lowered the kreatinin values in all cases studied. The error is fairly constant and averages ·00019 gram kreatinin per 10 cc., which is recommended as a correction factor.

The longer the solution stands, especially after adding the reagents, the lower is the kreatinin value. It is advisable to let stand five minutes after adding the reagents and read at once.

The presence of coagulable protein, also albumoses and peptones, lowered the values for kreatin and kreatinin, both alone and in meat extracts.

The autoclave method of Benedict and Myers modified so as to apply to meat products gave the most satisfactory results in determining kreatin.

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Zur Analyse von Wolframstahl.

Nach Versuchen von Dipl. ing. Th. Dieckmann.

Von. Prof. Dr. F. Willy Hinrichsen.

Zur Bestimmung von Wolfram und Chrom in Spezialstählen hat sich das folgende Verfahren gut bewährt: Man dampft den Wolframstahl mit Salpetersäure ein, schliesst den Rückstand mit Natriumsuperoxyd auf und zieht mit Wasser aus. Die so entstehende Lösung, welche sämtliches Wolfram und Chrom als Wolframat und Chromat enthält, wird im Maasskolben aufgefüllt. In einem Teil dieser Lösung fällt man sodann beide Elemente zusammen mit Merkuronitrat. Der Niederschlag wird abfiltriert, geglüht und gewogen. Auf diese Weise erhält man das Gesamtgewicht von Wolframsäure + Chromoxyd. In einem anderen Teile wird der Gehalt der Lösung an Chromat durch Titration, zweckmässig auf jodometrischem Wege, ermittelt und das Chromoxyd von der Summe in Abzug gebracht.

Bei dieser Behandlungsweise wird auch gleichzeitig der Gesamtphosphor durch das Merkuronitrat abgeschieden. Um die Menge des Phosphors zu bestimmen, kann man in der vorher erwähnten Lösung die Phosphorsäure mittelst Magnesiamischung in der Siedehitze nach Jörgensen fällen. Der so entstehende Niederschlag enthält nur geringe Mengen Wolframsäure. Um diese zu entfernen und zugleich um eine grössere Gewichtsmenge zur Wägung zu bringen, löst man die Magnesiafällung mit Salpetersäure vom Filter und scheidet nun die Phosphorsäure in bekannter Weise nach Finkener ab.

Wird die Phosphorsäurefällung unmittelbar aus der wolframathaltigen Lösung nach Finkener ausgeführt, so gehen stets erhebliche Mengen Wolframsäure in den Niederschlag über. Unter gewissen Umständen lässt sich jedoch das Mitfallen der Wolframsäure durch den Zusatz von *Weinsäure* verhindern. Die übrigen in der Literatur beschriebenen Verfahren zur Trennung von Wolframsäure und Phosphorsäure versagen unter den bei der Phosphorbestimmung im Wolframstahl vorligenden Bedingungen.

Remarks on the Analysis of Molybdenum.

By Dr. E. Collett, *Christiania.*

ABSTRACT.

It has been found that the existing, commonly employed methods for the determination of molybdenum in the natural sulphide of molybdenum generally do not give very reliable results. The author has worked upon the matter and found that the following method gives good, reliable results:—

The exceedingly well-powdered sulphide of molybdenum is oxydised by fuming nitric acid, the acid evaporated and the residue treated with concentrated sulphuric acid under evaporation of the same. The residue, containing a little sulphuric acid, is taken up in water and filtered. The contents of the filter are washed with water and ammonia. The combined solutions are precipitated with ammonia and filtered, then excess of sulphide of ammonia is added to the solution and, after filtering, boiled with hydrochloric acid, and the precipitated sulphide of molybdenum separated from the solution, which is then evaporated and the main part of ammonia-salts expelled. The residue is taken up in water, ammonia added, and then once more precipitated by sulphide of ammonia and hydrochloric acid. The precipitated sulphide of molybdenum is heated, in the Rose crucible, in a current of hydrogen to constant weight.

The Estimation of Volatile Matter in Fuels.

By Prof. E. J. CONSTAM, *Director of the Swiss Fuel-Testing Laboratory at Zürich.*

The estimation of volatile matter in fuels is a very simple operation. It consists in determining, by calcination in a platinum or porcelain crucible, the yield of coke, *i.e.*, the loss of weight in a small sample of fuel. The results, however, depend largely upon the method used. For purposes of comparison or classification of the different coals, the yield of volatile matter must be calculated upon the pure combustible substance (1, 2.)

Different analysts employ different methods giving different yields of coke. As the classification of coal is, to a certain extent, based upon the percentage of volatile matter, and as it is customary, in tenders and contracts for coal, to stipulate the percentage, the international adoption of a standard method for the estimation of volatile matter in fuels is of theoretical and practical importance.

No crucible method will give *yields of coke* which will invariably agree with those obtained under varying industrial conditions. But I shall be able to demonstrate that the *chemical composition* of ash-free crucible coke prepared from various kinds of fuel, by the method of the American Committee on Coal Analysis (2, 3, 12), closely resembles the composition of the combustible matter of metallurgical and gas-coke.

Without regarding the yield of coke, a standard method for the estimation of volatile matter would therefore have to meet the following requirements: It should be a rapid and convenient method, practicable for all kinds of fuel, and widely accepted. Duplicate estimations should give close agreement. The coke produced should be in the same state of carbonisation as industrial coke, nearly free from volatile matter.

In order to contribute towards the settlement of this important question I have not only made a comparison, with the help of my assistants (4, 5, 6, 7) of the relative yields of coke obtained by means of various methods (8, 9, 10, 11) used on the Continent of Europe, in Great Britain and in the United States of America, but we have also examined the chemical composition and calorific power of coke obtained from various fuels by different methods.

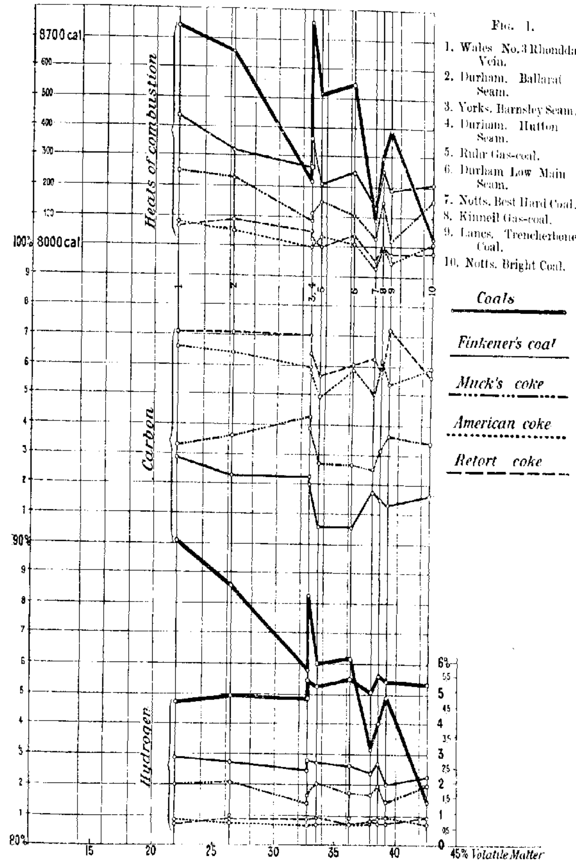
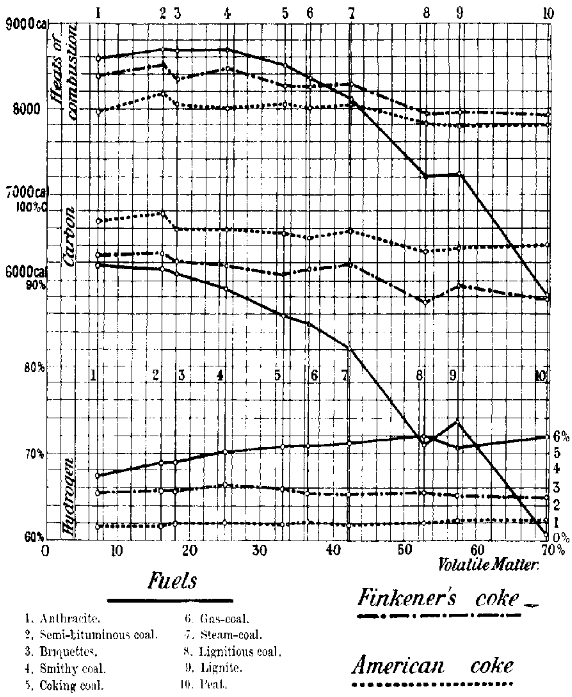


Fig. 1.

1. Wales No. 3 Rhondda Vein.
2. Durham. Ballarat Seam.
3. Yorks. Barnsley Seam.
4. Durham. Hutton Seam.
5. Ruhr Gas-coal.
6. Durham Low Main Seam.
7. Notts. Best Hard Coal.
8. Kinneil Gas-coal.
9. Lancs. Trencherbone Coal.
10. Notts. Bright Coal.

Fig. 2.


1 2 3 4 5 6 7 8 9 10
9000 cal
8000
7000 cal
100% C
6000 cal
90%
80%
70%
60%
Heats of combustion
Carbon
Hydrogen
6%
5
4
3
2
1
0%
0 10 20 30 40 50 60 70%
Volatile Matter.
Fuels
1. Anthracite.
2. Semi-bituminous coal.
3. Briquettes.
4. Smithy coal.
5. Coking coal.
6. Gas-coal.
7. Steam-coal.
8. Lignitious coal.
9. Lignite.
10. Peat.
Finkener's coke
American coke

Further, we have distilled, in a small gas-retort, at a constant temperature of 830° C., 1 lb. of each sample of coal used for our laboratory tests. The analysis and determination of the calorific value of the cokes so obtained proved them to be similar to metallurgical and gas coke.

The diagram No. 1 demonstrates the relation of the pure combustible matter of our retort cokes to that of the crucible cokes. It also shows the constituent parts of the specimens of British coal from which the cokes were prepared. The abscissæ indicate the percentages of volatile matter, determined by the American method, of the distilled coals. The ordinates show the percentages of carbon and of hydrogen, and heats of combustion, in calories, of the coals and the coke produced therefrom. The upper group of lines comprises the heats of combustion, the middle group the amounts of carbon, and the lower group the percentage of hydrogen in the coals and coke.

An examination of this diagram shows that pure coke obtained from different coals by Finkener's method (11) is more like the original coal than crucible coke prepared by the American method. The latter closely resembles the retort coke. Amongst the four kinds of coke represented in this diagram, the American and the retort coke have the lowest heat of combustion, the highest proportion of carbon, and the lowest percentage of hydrogen. This proves that their chemical composition closely resembles that of industrial coke.

Diagram No. 2 represents the heats of combustion and proportions of carbon and of hydrogen of different species of fuel, their volatile matter ranging from 7 to 70 per cent.; and also the corresponding values of the pure coke obtained therefrom by Finkener's and the American method, the former giving the maximum, the latter the minimum yield of coke. This diagram clearly shows that Finkener's coke is more like Anthracite than coke. On the other hand, the composition and heat of combustion of the American crucible coke appears to be independent of the nature of the fuel from which it was produced.

The comparison of the yields of coke obtained by different methods, with their *chemical composition*, proved that the highest yields were found by the method which gave the most coaly coke; whereas the lowest yields were obtained by the American method, which produces the most carbonised coke.

We were able to prove that the *crucible temperatures* differed according to the method employed. They were the same with the Bochum and the American methods. The latter, however, requires a longer heating of the coal than the former, and, therefore, produces a more carbonised coke.

We have been able to show, by special experiments, that in neither case was any part of the crucible coke burnt. Pyrometric observations showed that the increase of temperature was slower, and the final temperature of carbonisation lower in platinum crucibles which had become dull by use. This is the reason why more coke is found in such crucibles than in those which are kept bright. I am therefore led to assume that the different yields of coke obtained under different conditions are due primarily to the different degrees of carbonisation of the fuels tested. We found the chemical composition of ash-free coke to be independent of the composition of the distilled coal, and only dependent on the temperature and the duration of the distillation. We observed that the Finkener coke, obtained at 700° C., was more like coal, and weighed more than the Bochum and the American coke prepared from the same sample, both at a temperature of 900-910° C. The longer duration of carbonisation when using the American method results in a lower yield of coke of a very similar composition to that of industrial coke. For this reason, and considering that the latter method is applicable to all kinds of fuel, that duplicate results thereby obtained agree closely, and that this method is generally employed in the United States, and also in many of the leading laboratories of Great Britain, I wish to propose the international adoption of the American method as the *standard for the estimation of the yield of coke.* This method is described as follows (3):— Place one gram of fresh, undried, powdered coal in a platinum crucible, weighing twenty or thirty grams and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom six to eight cm. above the top of the burner. The flame should be fully twenty cm. high when burning free, and the determination should be made in a place free from draughts. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon."

In order to render results comparable, I propose as a *general definition for the yield of volatile matter* in fuels the percentage which

is found by subtracting from one hundred the yield of coke obtained, by the method of the American Committee on Coal Analysis (2, 3, 12) from 1 gram of fuel, in a bright platinum crucible. The yield must always be calculated upon the pure combustible matter.

The variations in the results found in different laboratories will, as a rule, be less than 1 per cent., and will rarely reach 2 per cent.

NOTES.

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2. Seyler. The Chemical Classification of Coal, Proc. of the Sth. Wales Inst. of Engineers. Vol. 21, p. 495; Practical Coal Mining, p. 77; Analyses of British Coals and Coke, 1907, p. IV,

3. Journ. Amer. Chem. Soc. Vol. 21, p. 1122. Butterfield, Chemistry of Gas Manufacture, Vol. I, p. 31.

4. Constam u. Rougeot. Zeits. f. angew. Chemie, XVII, No. 23; Glückauf, 1906, No. 15.

5. Constam u. Schläpfer. Gas Journal, 1906, p. 741 ff.

6. Streit. Dissertation, Zürich, 1906.

7. Kolbe. Dissertation, Zürich, 1908.

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9. Mahler. Etudes sur les Combustibles, 1903, p. 83.

10. Goutal. Annales de Chimie analytique, 1903, No. 1, Gas Journal, 1905, p. 1006.

11. Hinrichs u. Taczak. Glückauf, 1908, p. 1325 ff.

12. Strahan and Pollard The Coals of Sth. Wales, Memoirs of the Geol. Survey, London, 1908, p. 7.

Discussion.

Prof. E. J. Constam:—I propose as a *general definition for the yield of volatile matter in fuels* the percentage which is found by subtracting from one hundred the yield of coke obtained by the method of the American Committee on Coal Analysis,* from 1 gram of fuel, in a bright platinum crucible. The yield must always be calculated upon the pure combustible matter.

Dr. L. J. Terneden (Amsterdam) said:—I feel very interested in the paper read by Professor Constam, and I am glad that Professor Constam has been so kind as to inform us of his proposition in connection with fuel-testing. The Society of Gas Engineers in Holland delegated me to this Congress, as during the past years we ourselves have been endeavouring to arrive at international methods of fuel-testing.

* Journal Amer. Chem. Soc., Vol. 21, p. 1122.

As a delegate from gas works, it is obvious that I have no objection to the proposed American method of coke-testing; the results of this method being nearest to those obtained in our works; and even before I had the pleasure of hearing Professor Constam's communications, I had decided to second, in the name of the Dutch Society of Gas Engineers, the proposition made.

The coke test is a small part of fuel-testing, giving us the amount of coke and volatile matter, and leaving us ignorant of the nature of the coke to be expected. But you will agree that it is better to do one step in the right direction than to remain stationary. However, fuel-testing is so important that we must go further, and try to get agreement on all points. Even though some parts of fuel-testing do not give rise to differences of opinion, no one can say that fuel-testing and valuation of fuel are complete.

Therefore we think it good to form a special committee to discuss matters extensively, to make tests, and to endeavour to come to an agreement. Such a commission appointed by the authorities concerned in the different countries could do good work. This commission should be permanent and international, and should deal with fuel as extensively as possible.

Professor C. Blacher (Riga):—Bei der Koksausbeute erhält man sehr sichere Werte, wenn man den sich im Platintiegel bildenden Kohlenstoffansatz vollständig ausschüttet, indem man die Kohle (in Form eines Briketts) in ein kleines halbkugelförmiges zweites Platinschälchen legt und den Kohlenstoffumsatz auf diese Weise nicht mitwiegt. Für eine allgemein vorzuschlagende Methode der Koksausbeute war diese Arbeitsart vielleicht zu kompliziert, meine Erfahrungen deuten jedoch darauf, dass die Menge des Ansatzes an Abhängigkeit von der Temperatur stark schwankt und daher auch die Höhe der Flammen genauer bestimmt werden müssten, damit keine Versehen hierin gemacht werden können. Damit man nun ja keine zu kleine Flamme nimmt, bei welcher der Deckel kälter bleiben kann, scheint es mir nötig zu sein sicherheitshalber eine grössere Flammenmasse festzusetzen.

Bei Ausschaltung des Koksansatzes habe ich durch Bestimmung der flüchtigen Bestandteile bei verschiedenen Temperaturen sogar platt verlaufende Kerzen erhalten.

Dr. R. Lessing pointed out that in the process of coking the secondary decomposition of volatile constituents must not be lost sight of. These explained the higher coke yield in a dull platinum crucible as against a bright one, by reason of the higher catalytic action of the former. On account of the secondary decomposition he felt inclined to prefer weighing the crucible without the lid. He should like to congratulate the U.S.A. Geological Survey on the excellent work carried out in their Fuel-testing Department.

Mr. W. H. Patterson discussed the influence of using a new platinum crucible for the determination, an older crucible being roughened by hydrocarbon fuels from the coal gives different amounts of coke. He quoted the method of the "Versuchsanstalt," Karlsruhe, of carrying out the determination by heating the coal in the crucible over a Bunsen flame until one minute after the flame of the coal gas is extinguished and good comparable results thereby obtained.

Mr. Arthur H. Lymn said:—I would support the suggestion that the proposed commission should deal with the whole analysis of fuels, instead of being limited to volatile matter and coke. I am a victim of these variations in coal analyses, hundreds of which come to me from all over the world, and I consider that standardisation would be a boon to the whole commercial world.

I propose that this commission should also include gentlemen who are interested in the commercial utilisation of coals, so that sharp and quick methods suitable for technical commercial laboratories may also be fixed as standards.

Professor Bosshard (Zurich) unterstützt den Vorschlag Professor Constams, da die vorgeschlagene Methode sich durch Einfachheit und Zuverlässigkeit auszeichnet.

Mr. G. Nevill Huntly stated that after comparing the published methods for the determination of volatile matter in coal, he adopted the American method as being the most uniform and consistent. The determination was essentially empirical, and the most consistent method was the best. The results of Professor Constam supply additional reasons for this method, and remove some of the objections to a purely empirical estimation. The testing of 1 gram samples, representing bulk samples of 100 tons or more, was always regarded by engineers in this country with suspicion. This suspicion is unfounded, as large coal can be sampled by hand to within 1 per cent.,

and small slack to 0·5 per cent., and with special sampling machinery this error can be reduced.

Dr. J. T. Dunn (Newcastle-on-Tyne) said:—I wish to support Dr. Constam's proposal. For many years our laboratory has determined the volatile matters in coal by placing the crucible in a muffle heated to 1000° C., but of late I have been comparing this method with the American method, not over such a great variety of fuels as Dr. Constam, but over coals varying very considerably in their content of volatile matter, and have found closely concordant results. These results, too, agree very closely in the case of gas-coals with the results of gas-making tests, in which $2\frac{1}{4}$ lbs. of coal are coked, and in which the coke closely resembles industrial gas-coke.

The great convenience of the American method is a strong recommendation; but if it be recommended by this Congress for international adoption, it would be well to specify whether the crucible should be weighed with or without the lid, as the carbon on the underside of the lid is sufficient to affect the result.

Technical Coal Analysis.

By Edward Gudeman, Chicago, Illinois.

Paper discusses the wants and needs of the stationary boiler plant proprietor in regard to coal analysis. The purposes of such technical analyses are given as two-fold, to judge the product itself and to give the consumer information as to its value directly in money value compared with a standard product, or based on efficiency for actual usage.

Paper considers that too many unsuitable determinations are now made and required by the analyst and that too much importance is given to valuation based on determination of B.T.Us.

Paper considers that determination of loss on drying under fixed and specific conditions, determination of volatile matter, fixed carbon, ash and sulphur and calculation of efficiency are fully sufficient to grade and value coals used for steam production in stationary boiler plants. Paper is confined to conditions found in the United States, in steam plants where daily consumption does not exceed 50 tons of coal.

Méthode simplifiée et Appareil nouveau pour déterminer le Pouvoir calorifique des Combustibles gazeux.

Par M. P. Lemoult, *Université de Lille.*

Résumé.

La méthode est basée sur cette remarque que l'on peut évaluer à l'aide d'une formule simple qui est la suivante: $P = a.0,909 + b.3,418$ le pouvoir calorifique P d'un mélange combustible contenant H^2, CO et CH^4 comme " gaz utiles " en mesurant: (1) la contraction produite par la combustion suivie de l'action d'une lessive alcaline; c'est *a*; (2) la consommation d'oxygène; c'est *b*.

Cette formule elle-même est basée sur une remarque simple, à savoir que par leur contraction, leur consommation d'oxygène, aussi bien que par leur pouvoir calorifique; $69^{Cal.}$ et $68^{Cal.2}$ la molécule H^2 et la molécule CO ont entre elles la plus grande ressemblance, au point que dans un mélange gazeux à 3 inconnues x, y et z, teneurs respectives en H^2, CO et CH^4 il n'y a à considérer que deux inconnues, à savoir $x+y$ et z. Ceci simplifie l'étude calorifique de ces mélanges et permet l'établissement pour évaluer P d'une formule à deux termes comme celle qui figure ci-dessus. Quand les mélanges gazeux contiennent d'autres combustibles, comme C^2H^4, C^6H^6, etc. . . il n'y a pas lieu d'en tenir spécialement compte; en effet dans les mélanges gazeux usuels, la teneur de ces combustibles supplémentaires varie dans des proportions assez faibles et en tenant compte de l'erreur qui en résulte comparativement au pouvoir calorifique des dits mélanges, on voit que cette erreur n'atteint pas 2 pour cent; or c'est l'erreur que l'on commet ordinairement avec les appareils les plus perfectionnés comme les bombes calorimétriques.

Pour mesurer *a* et *b* dans des conditions industrielles, loin du laboratoire, et avec une précision suffisante, j'ai imaginé un appareil formé d'un tube mesureur, d'une petite bombe où les combustions se font avec une sécurité parfaite et d'un réservoir d'attente en verre où une partie du mélange gazeux et d'oxygène est mise momentanément en réserve pour déterminer, à la fin de l'expérience, l'oxygène contenu; on mesure la contraction, puis l'oxygène, qui reste après combustion; on a donc ce qu'il faut pour évaluer *a* et *b*.

Quant à l'oxygène nécessaire aux combustions, il est fourni par une préparation spéciale, la Sodoxylithe, qui donne dans l'appareil même et en quantité voulue le gaz oxygène dont on a besoin.

A titre d'exemple, le gaz d'éclairage de la Ville de Lille, prélèvé le 13 Mars 1909 avait un pouvoir calorifique de 5007 Cal. par mètre cube à 0° et 760 mm. Il contenait*

Hydrogène + Oxyde de carbone	65,8%
Méthane	31,1%
Azote	3,1%

Pouvoir calorifique (déterm. par la bombe Berthelot) 5032 Cal.

L'appareil est conçu de manière à avoir les dimensions les plus réduites et se transporte facilement.

M. Georges Cottin read a Paper on

Unification des Méthodes en Chimie Analytique, Microscopie et Bactériologie Médicale.

* L'anhydride carbonique préalablement enlevé atteignait 3 pour cent.

Sur l'emploi des raies ultimes dans l'analyse spectrale appliquée à la chimie.

Par A. DE GRAMONT.

J'AI déjà résumé† dans les Comptes Rendus du Quatrième Congrès International de Chimie appliquée (Paris, 1900) une partie des recherches que je poursuis, depuis plusieurs années, sur les spectres de dissociation des composées chimiques. Je rappellerai que ces spectres de lignes obtenus avec les solides conducteurs, les sels fondus, ou les précipités en suspension dans ceux-ci, sont produits par l'étincelle de décharge d'un condensateur électrostatique (une ou plusieurs jarres de Leyde de 0·002 à 0·02 microfarad) intercalé dans le secondaire d'une bobine d'induction. Les éléments constitutifs du composé sont ainsi libérés et donnent chacun son spectre de lignes où les métalloïdes, aussi bien que les métaux, sont représentés par leurs raies caractéristiques.

Plus récemment‡ un procédé de simplification des spectres complexes, et d'élimination de certaines classes de raies, m'a été fourni par les belles recherches de MM. Schuster et Hemsalech§ sur l'étincelle rendue oscillante par l'intercalation d'une self-induction dans le circuit de décharge. Le spectre de l'air disparaît d'abord, puis les spectres de la plupart des métalloïdes ; les raies qualifiées de "haute température," ou "raies courtes" des métaux dans l'étincelle ordinaire s'affaiblissent jusqu'à disparaître et les lignes communes à l'arc et à l'étincelle deviennent plus vives, de sorte qu'on finit par obtenir un spectre assez voisin de celui de l'arc. L'emploi de la self-induction m'a donc permis une sorte de séparation analytique des éléments, et une simplification progressive, certainement avantageuse, de leurs spectres. Au cours de ces recherches j'ai relevé dans les spectres des minéraux, et dans ceux des alliages, les lignes qui représentent les corps simples en faibles quantités ou à l'état de traces, et j'ai désigné, par le terme de "*Raies Ultimes*"

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† "Sur l'application de l'analyse spectrale à la chimie analytique," par M. A. de Gramont. Voir aussi "Analyse spectrale directe des Minéraux," vol. 1, Paris, Baudry, 1894, et "Bulletin de la Société chimique," 3ᵉ série, t. 13 (1895) ; t. 17 (1897) ; t. 19 (1898).

‡ Comptes Rendus de l'Académie des Sciences, t. 131 (1902), p. 1048 ; 1205.

§ Phil. Trans., t. 193 (1899), p. 189 ; et Hemsalech, Thèse de doctorat, Paris, 1901.

celles qui disparaissent les dernières et qu'il faudra rechercher pour déceler un corps, parce qu'elles offrent le maximum de sensibilité. Les raies ultimes ne sont pas nécessairement les plus fortes, mais celles qui résistent à l'effet de la self-induction, ou qui se rencontrent dans l'arc, et même dans la flamme du chalumeau oxyhydrique. En réalité la diminution de la teneur d'un corps dans une source lumineuse modifie le spectre de lignes de ce corps comme le ferait un abaissement de température, ou, si l'on préfère, une diminution de l'énergie vibratoire de l'atome ou des électrons de cette source. Cette indication générale ne s'applique plus aux régions les moins chaudes des flammes où souvent les raies les plus sensibles des températures supérieures ne sont plus représentées, et où d'autres raies, correspondant sans doute à des groupements constitutifs plus stables dans ces conditions, deviennent, alors seulement, caractéristiques des faibles teneurs. Je citerai par exemple λ 4226·9 du calcium et λ 4607·5 du strontium, dans la flamme ordinaire du bec Bunsen.

Les considérations qui précèdent faisaient prévoir une répartition possible des métalloïdes, au point de vue des raies ultimes, en deux groupes :

1° Métalloïdes donnant des spectres d'arc et susceptibles de présenter, dans l'étincelle condensée, des raies ultimes peu nombreuses et sensibles : tellure, phosphore, arsenic, antimoine, carbone, silicium, bore.

2° Métalloïdes dont on n'a pu jusqu'ici obtenir de spectres d'arc et dont le spectre d'étincelle disparaît rapidement avec la diminution de leur teneur dans un composé, les raies les plus fortes persistant à peine plus que les autres : fluor, chlore, brôme, iode, oxygène, soufre, sélénium, azote.

J'ai pu vérifier en effet l'exactitude de cette répartition des métalloïdes.† Les raies ultimes de ceux du premier groupe sont situées dans la partie la plus réfrangible de l'ultra violet.

Les spectres des corps simples étaient obtenus, pour la partie visible, en premier lieu par l'observation oculaire avec un spectroscope, à deux prismes, et en second lieu photographiés avec des plaques panchromatiques Wratten avec un spectrographe à prisme composé Rutherfurd en flint très dispersif et à objectif achromatique de 40 cm. de foyer ; le spectre ainsi obtenu s'étendait depuis

† Comptes rendus, t. 146, 15 juin 1908.

environ λ 7000 dans le rouge jusqu'à λ 3500 dans le commencement de l'ultra violet. Pour les recherches dans l'ensemble de l'ultra violet, j'ai fait usage d'un spectrographe à partie optique (prisme Cornu et lentilles simples) toute en quartz, avec objectifs de 40 cm. de foyer, et les études entreprises avec cet appareil ont porté depuis λ 5000 dans le vert jusqu'à λ 2000 environ, à l'extrémité de l'ultra violet, laissant ainsi une région commune du spectre pour le raccordement des clichés obtenus avec les deux spectrographes flint et quartz. Dans certains cas et pour augmenter la dispersion dans l'ultra violet j'ai substitué un prisme de spathcalcite à celui de quartz, mais, à cause de l'absorption du spath, le spectre ne s'étendait que jusqu'à λ 2170 dans l'ultra violet.

Les raies les plus persistantes des spectres d'étincelle des solutions étudiées par Mr. Hartley,† puis récemment par MM. Pollok et Léonard,‡ sont en général les mêmes que les raies ultimes des spectres de dissociation. Les quelques divergences que j'ai reconnues me paraissent tenir surtout à ce fait que les spectres des solutions n'ont point été étudiés au delà de λ 2540 dans l'ultra-violet tandis que les spectres recueillis sur mes clichés s'étendent jusqu'à λ 2000.

J'ai employé des fentes en nickel, dont l'ouverture était de 20 μ ou 25 μ. Les diverses self-inductions essayées ont varié de 0·0001 à 0·1 Henry et ont été, soit mesurées par la méthode de Lord Rayleigh, ou de Stroud et Oates, soit calculées par la formule de Perry.

Voici d'abord les raies ultimes,§ et les raies les plus sensibles après celles-ci, pour les métalloïdes :

Tellure.—Le doublet *2385·9* ; 2383·4 dans l'ultra violet.

Phosphore.—Les deux doublets 2555·0 ; *2553·4* ; et *2535·8* ; 2534·1 dans l'ultra violet.

Arsenic.—Les raies 2780·4 ; 2349·8 ; *2288·2* dans l'ultra violet.

Antimoine.—Les raies *2598·2* ; 2528·6 ; *2311·6* dans l'ultra violet.

Carbone.—La raie 2478·7 dans l'ultra violet. La raie indigo 4267·0 est assez sensible.

Silicium.—Les raies *2881·7* ; 2528·6 ;‖ 2516·2 dans l'ultra violet, les deux dernières faisant partie d'un groupe bien caractéristique de six raies.

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† Researches on Spectrum Photography, Phil. Trans., London, 1884.

‡ Scient. Proc. Roy. Dublin Soc., t. xi. July, 1907.

§ Les raies ultimes sont imprimées en caractères *italiques*.

‖ Cette raie ne doit pas être confondue avec celle de l'antimoine qui paraît avoir même longueur d'onde.

Bore.—Le doublet 2497·8 ; 2496·8 dans l'ultra violet. Elles paraissent facilement confondues, si la fente n'est pas fine. Je n'ai pu déterminer quelle est la plus sensible des deux.

Un grand nombre de métaux donnent des raies ultimes persistant pour des teneurs extrêmement faibles et très inférieures à celles pour lesquelles l'ensemble de leur spectre a disparu. Quelques lignes que je présente ici diffèrent de celles que j'ai données primitivement† parce que dans ce premier travail j'ai parfois indiqué un groupe de quelques raies au lieu de la plus sensible de celles-ci ; par exemple pour le fer.

Lithium.—*6708·2* dans le rouge, et 4602·6 dans le bleu, plus facilement photographiable.

Sodium.—Le doublet jaune bien connu *5896·2* ; *5890·2*, et le doublet ultra violet 3303·1 ; 3302·5, plus facilement photographiable.

Potassium.—Le doublet violet *4047·4* ; 4044·3.

Rubidium.—Le doublet indigo 4215·7 ; *4202·0*.

Cæsium.—Le doublet bleu 4593·4 ; *4555·4*.

Toutes ces raies des métaux alcalins ont aussi été reconnues par Mr. Hartley comme les plus sensibles dans la flamme.

Calcium.—Les raies H et K Frauenhofer 3968·6 ; *3933·8*.

Strontium.—Les raies violettes, 4215·7 ; 4077·9.

Baryum.—Les raies vertes 5535·7 et 4934·2 et la raie bleue *4554·2* plus facilement photographiable ; la raie ultra violette 2335·4 paraît très sensible aussi.

**Radium.*—D'après les travaux de Runge et Precht il semblerait que la raie la plus sensible soit 3814·6 dans le commencement de l'ultra violet.

Magnésium.—Les raies ultra violettes 2795·6 ; 2802·8 ; *2852·2*.

Zinc.—Les raies ultra violettes *3345·2*, 3303·1 ; le triplet bleu bien connu est très sensible aussi.

Cadmium.—Les raies ultra violettes 2288·1 ; *2265·1* ; 2144·4 toujours présentes dans le zinc. Les raies verte 5086·1 et bleue 4800·1 sont très sensibles à l'œil.

**Glucinium.*—Je n'en ai pas repris l'étude, mais dans la partie visible la raie bleue 4572·9 m'avait autrefois paru sensible.

Fer.—Les raies ultra violettes 2739·6 ; 2631·1 ; 2599·5 ; 2598·5 ;

† Comptes rendus, t. 144, p. 1101 (21 mai 1907). Une partie seulement des corps dont je donne ici les raies ultimes étaient étudiés dans cette note.

* Ce signe indique les corps que j'ai incomplètement étudiés encore, ou que je cite d'après des observations étrangères.

2395·7 ; *2382·2* ; et dans la partie visible 4383·7 ; 4045·9 sensibles surtout par la photographie.

Nickel.—Les raies ultra violettes 2437·9 ; *2416·2* ; 2316·1.

Chrome.—Dans la région visible : le triplet vert 5208·6 ; 5206·2 ; 5204·7 est le plus sensible à l'œil, et le triplet indigo 4289·9 ; 4275·0 ; 4254·5 par la photographie. Pour l'ensemble du spectre : 3605·5 ; 3593·6 ; 3578·8.

**Manganèse.*—Dans le violet le doublet *4030·9* ; *4033·2* surtout sensible par la photographie. Pour l'ensemble du spectre : 2605·8 ; 2593·8 ; *2576·2*.

Aluminium.—Le doublet du commencement de l'ultra violet, visible encore, *3961·7* ; 3944·2.

**Gallium.*—Les raies violettes 4171·8 ; 4032·7.

**Indium.*—La raie bleue surtout 4511·4 et la raie violette 4102·0.

Étain.—Les raies ultra violettes 3262·3 et *2863·3* ; la raie bleue 4524·9 est sensible.

Bismuth.—Les raies ultra violettes *3067·8* ; 2898·1 ; et 2938·4, et aussi la raie bleue 4722·7 moins sensible.

Germanium.—Les raies ultra violettes *3039·2* et 2651·4 ; l'orangée et la jaune, si caractéristiques, offrent fort peu de sensibilité.

**Molybdène.*—Les raies ultra violettes 3903·1 ; *3864·2* ; *3798·4*.

Cuivre.—Dans l'ultra violet le doublet 3274·1 ; *3247·7* et la raie 2369·9. Dans le vert, les trois raies vertes bien connues sont très sensibles à l'œil, surtout : 5105·7 et 5218·4.

Argent.—Dans l'ultra violet le doublet 3383·0 ; *3280·8* et la raie 2437·9. Dans le vert les deux raies 5209·2 et surtout 5465·6 sont fort sensibles.

Mercure.—Les deux raies ultra violettes 2848·0 et *2536·7* m'ont paru être les plus sensibles ; la dernière est la seule raie du Mercure qui ait pu être obtenue dans la flamme par M. de Watteville.

Or.—Les raies ultra violettes *2676·0*, et 2428·0. Elles se voient dans presque tous les boutons d'argent de coupellation.

Je poursuis actuellement ces études, spécialement en ce qui concerne les corps ci-dessus marqués d'une *, et pour ceux qui n'ont pas été cités, mais dont plusieurs tels que l'uranium ne paraissent pas donner de raies de grande sensibilité.

* Ce signe indique les corps que j'ai incomplètement étudiés encore, ou que je cite d'aprè des observations étrangères.

Ueber einige komplexe Aluminioorganische Verbindungen.

Von Jos. Hanuš und Ot. Quadrat.

Manchen organischen Verbindungen, wie den mehrwertigen Alkoholen, Oxysäuren, etc., kommt die Eigenschaft zu, die Ausfällung vieler Metalle, namentlich Cu, Al, Fe, Mn, Zn und Ni, in unlöslicher Form aus ihren wässerigen Lösungen durch OH′, CO_3'', PO_4''', etc. Ionen zu verhindern. Nach jetzigen modernen Anschauungen handelt es sich hier um gewisse ziemlich beständige Komplexe, deren Studium, sowie ihrer Entstehungsbedingungen, ohne Zweifel für die analytische Chemie von hohem Belang ist. Die Verhältnisse, bei welchen die Ausscheidung aufhört, sind aber für jede Metalllösung, sowie für jede organische Oxyverbindung, verschieden, sodass sie für jedes Metall besonders ermittelt werden müssen. Wir haben uns also die Aufgabe gestellt, das Verhalten der organischen Oxyverbindungen bei der Ausscheidung des Aluminiums aus seinen wässerigen Lösungen als $Al(OH)_3$ durch Ammoniak einem gründlichen Studium zu unterziehen und dies um so mehr, als die literarischen Angaben über diesen Gegenstand nur sehr selten und allgemeiner Natur sind. (Siehe *Méhu*, Jahresbericht über die Fortschr. d. Chemie, 1873, S. 569, *Grossman-Schück*, Chem. Ztg. 31, [1907], 911, und *Strecker*, Chem. Ztg. 31 [1907], 1217, sowie eine zeitgemässe Zusammenstellung aller Forscher, die sich von allgemeinem Standpunkte mit betreffendem Thema beschäftigt haben, in *Roszkowski's* Mitteilung, Z. anorg. Ch. 14, 1 [1897]; die Konstitution der hierbei auftretenden Komplexe studirten, *Kahlenberg*, Z. f. phys. Ch. 17 [1895], 577, *Wohl*, *Stolle*, Centrbl. f. Zuckerind. 1904, 32, u.s.w.).

Durch systematisches Studium ist man zur Erkenntnis gekommen, dass die Eigenschaft, die Ausfällung der Metalle zu verhindern, denjenigen Substanzen eigen ist, die mehrere Hydroxylgruppen enthalten; ersetzt man diese Gruppen mit anderen (NH_2, Cl, I, u.s.w.), so entbehrt die neuentstehende Substanz der erwähnten Eigenschaft (Roszkowski).

Unsere eigenen Versuche betreffs des Aluminiums zielen zur Beantwortung folgender Fragen:—

(1) In welchem Masse ist die Ausfällung des $Al(OH)_3$ von der Menge der anwesenden Oxyverbindungen abhängig?

(2) Verhalten sich gegen Aluminium alle Oxyverbindungen gleich und bestätigen sich auch hier die Befundnisse Roszkowski's beim Ersatze der wirksamen (OH) Gruppen durch eine andere Funktionsgruppe?

(3) Lassen sich die vermuteten Komplexverbindungen isolieren und was für eine Konstitution ihnen gebührt?

Die Versuche wurden mit folgenden Oxyverbindungen angestellt: Tartronsäure, Aepfel-, Wein-, Zucker-, und Zitronensäure, Weinsaures Kalium-Natrium, weinsaures Ammonium, Milchsäure, Glycerinsäure und Glycerin. Es wurden von allen diesen Stoffen 2/5 *n*-Lösungen bereitet. Von den Aluminiumsalzen wurde das Aluminiumsulfat genommen (in 5 cm^3 0·0271 g. Al).

Verwendet wurde folgende Beobachtungsmethode: Es wurden versuchsweise diejenigen Mengen von Oxysäurelösungen ermittelt, die verursachen, dass stets dasselbe Volumen der Aluminiumsalzlösung mit stetigem Volumen Ammoniaks opalisiren aufhört, d.h. nicht mehr gefällt wird. Es ist uns auf diese Weise gelungen, die Grenze der Nichtfällbarkeit bis auf 0·1 cm^3 der 2/5 *n*-Säurelösung, also bis auf 0·8 %, genau zu bestimmen. Wir sind zu folgenden in molekularen Proportionen ausgedrückten Ergebnissen gelangt:

Oxysäureverbindung.	Gefundenes Grenzverhältniss Al : Oxyverbindung.	Nähert sich dem Verhältnisse
Tartronsäure	4 : 2·99	4 : 3
Aepfelsäure	4 : 3·02	4 : 3
Weinsäure I. ..	4 : 2·52	4 : 2·5
Al-lösung angesäuert II. ..	4 : 2·48	4 : 2·5
Al-lösung ungesäuert III. ..	4 : 2·50	4 : 2·5
Weinsaures K–Na	4 : 2·52	4 : 2·5
„ Ammonium ..	4 : 2·54	4 : 2·5
Zuckersäure	5 : 2	5 : 2
Zitronensäure	4 : 1·5	4 : 1·5

Die Milchsäure auch in sehr grossem Ueberschuss ist nicht imstande, die Ausscheidung des Aluminiums zu verhindern, ebenfalls die Glycerinsäure ist nicht fähig das Aluminium für das

Verhältniss 3 At. Al. : 32 Mol. Glycerinsäure vollständig in Lösung zurückzuhalten. Auch das Glycerin hat die genannte Fähigkeit stark eingebüsst, so dass es in seiner Wirkung nicht den Oxysäuren gleichgestellt werden kann.

Man kann also sagen: Die Fähigkeit, die Ausscheidung des Al als $Al(OH)_3$ aus seinen wässerigen Lösungen durch NH_3 zu verhindern oder die Tendenz mit Al ziemlich beständige komplexe Verbindungen zu bilden, fängt in grosserem Masse erst bei solchen Stoffen an, die neben einer alkoholischen Gruppe wenigstens zwei Karboxylgruppen enthalten; sie fehlt aber solchen Substanzen, die blos eine OH neben einer COOH-Gruppe ausweisen; im geringeren Masse tritt sie bei denjenigen Substanzen auf, die mit 3 OH-Gruppen oder mit 2 OH und einer COOH-Gruppe versehen sind.

Im weiteren suchten wir die Bedeutung der OH- sowie COOH-Gruppen gründlich zu erklären. In dieser Hinsicht haben wir den von Roszkowski teilweise eingeschlagenen Weg gewählt, und zwar, die unvermeidliche Notwendigkeit der Anwesenheit von OH-Gruppen haben uns die Versuche mit Amino- ($COOH.CH_2.CHNH_2.COOH$), Monobrom- ($COOH.CH_2.CHBr.COOH$), und Methoxybernsteinsäure ($COOH.CH_2.CHOCH_3.COOH$) gezeigt und die notwendige Anwesenheit von Karboxylgruppen wurde durch Versuche mit Säure-anhydriden (Weinsäureanhydrid) und -Hydraziden (Aepfelsäurehydrazid) bewiesen.

In Gegenwart von allen oben angeführten Bernsteinsäurederivaten in den oben für Aepfelsäure ermittelten Grenzverhältnissen hoch überlegenen Mengen, wurde stets das Aluminium quantitativ durch NH_3 ausgeschieden.

Besonders Versuche mit Methoxybernsteinsäure (*Purdie*, Journ. Chem. Soc. 59, 468) haben nachdrücklich gezeigt, dass bei Komplexbildung dem H in OH-Gruppe eine sehr wichtige Rolle zuerkannt werden muss.

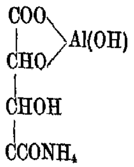
Aber auch bei Anwesenheit von Weinsäureanhydrid und Aepfelsäurehydrazid, in welchen also freie Karboxylgruppen nicht auftreten, wurde das Al durch NH_3 ausgeschieden.

Man kann also behaupten, dass auch die Gegenwart von Karboxylgruppen, nicht der Hydroxylgruppen allein, beim Hervorrufen metalloorganischen mittels NH_3 nicht fällbaren Komplexverbindungen, wenn auch in ein wenig kleinerem Masse als jene der OH-Gruppen, mitwirkt.

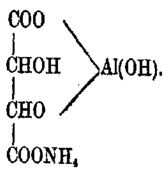
Bei den Versuchen mit Brombernsteinsäure haben wir auch bewiesen, dass diese Säure in neutraler oder schwach ammoniakalischer Lösung sukzessiv in Aepfelsäure umgewandelt wird, welche Erscheinung den Reaktionsverlauf sehr beeinflusste.

Es ist uns auch gelungen das Aluminiumweinsäure- und Aluminiumtartronsäurekomplex auf folgende Weise zu isoliren. Die kalte, deutlich ammoniakalische Lösung von Aluminiumnitrat und Weinsäure bzw. Tartronsäure (im molekularen Verhältnisse) wurde mit gleichem Volumen 96 %-igen Alkohols gefällt, der weisse Niederschlag abgesaugt und auf porösem Teller getrocknet; die durchsichtig und gummiartig gewordene Masse wurde fein zerrieben, mit 50 %-igen Alkohol gründlich nachgewaschen und über Chlorcalcium getrocknet.

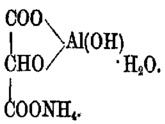
Die Analyse führte zu folgenden Konstitutionen :—
bei Weinsäure:



oder



bei Tartronsäure;



Die isolirten Substanzen haben auch ausgeprägten Charakter einer Komplexverbindung. Ihre wässerigen Lösungen werden weder mit NH_3 noch mit Ammonsulfid und Natriumphosphat gefällt. Erst wenn die Lösung mit $n/10$ NaOH entsprechend der anwesenden Weinsäure bzw. Tartronsäure 18–20 Min. lang erhitzt wird, beginnt sie zu opalisieren und bei weiterem Kochen einen Niederschlag (etwa 78% des vorhandenen Aluminiums) abzusetzen.

Die Isolation der Aepfel- und Zitronensäurekomplexe ist fehlgeschlagen.

Schlussfolgerungen.

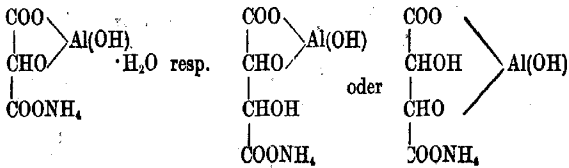
Die Eigenschaft mancher organischen Oxyverbindungen in wässerigen Lösungen mit Aluminium zu komplexen Verbindungen eingehen, infolgedessen die Ausscheidung dieses Metalles durch

Ammoniak eingebüsst ist, wurde einem gründlichen Studium unterworfen.

Die Fähigkeit zur Komplexbildung *hängt nicht nur von der Zahl der* OH *sondern auch jener der Karboxylgruppen ab*; *sie kommt also erst bei denjenigen Verbindungen im merklichen Masse zum Vorschein, die mindestens* 2 COOH *neben einer* OH-*Gruppe* (Tartron u. Aepfelsäure) ausweisen; Stoffe mit zwei OH und einer COOH-Gruppe oder die blos drei OH-Gruppen enthalten, üben die genannte Eigenschaft erst bei sehr hohen Koncentrationen aus (Glycerinsäure und Glycerin). Daraus kann man den Schluss ziehen, dass an der Bindung des Metalles in den entsprechenden Komplexen nicht nur die OH sondern auch Karboxylgruppe teilnimmt.

Einer jeden organischen Oxyverbindung entspricht ein gewisses Grenzverhältniss, bei welchem die Ausscheidung des Metalles durch Ammoniak total aufhört, und welches je enger ist, desto mehr OH und COOH-Gruppen nebeneinander in den betreffenden Oxyverbindungen vorkommen.

Den von Tartron- und Weinsäure isolierten komplexen Aluminiumsalze wurden die Formeln:



beigelegt.

The Solution Densities of Dextrose, Lævulose and Maltose.

By Arthur R. Ling, F.I.C., Lewis Eynon, B.Sc., F.I.C., and J. H. Lane, A.I.C.

The authors have prepared the three sugars above-named in a state of high purity, the criterion of the latter being constancy of specific rotatory power under standard conditions of temperature and concentration. The following values were obtained with the final products, expressed in each case on the anhydrous sugars:

Dextrose	...	$[\alpha]_{D\,17^\circ}$ + 52·72° (c=10).
Lævulose	...	$[\alpha]_{D\,18{\cdot}5^\circ}$ − 93·83° (c=10).
Maltose	...	$[\alpha]_{D\,17{\cdot}5^\circ}$ + 137·79° (c=5·7).

The specific gravities of solutions of these preparations, varying in concentrations from c = 1 to c = 24, have been determined in duplicate. The results practically confirm those of Brown, Morris, and Millar (J. Chem. Soc. Trans., 1897, **71**, 77, 276), and the excuse for publishing them rests mainly on the fact that the purity of the various sugars employed is beyond all question, and that a considerably larger number of determinations have been made. Brown and Morris (*loc. cit.*) co-ordinated the specific gravities of the sugar solutions and the corresponding solution densities. In this way they expressed their results in the form of a curve. The authors point out that, although the actual law may be a curve, for all practical purposes, the results may be represented graphically by a straight line.

In the following tables containing the mean results:—

Column (*A*) gives the weight of dry substance taken.

Column (*B*) gives the total weight of solution.

Column (*C*) gives the specific gravity of the solution at 15·5°, referred to water at the same temperature.

Column (*D*) gives the grams of sugar per 100 reputed cc. (fluid grams at 15·5°).

Column (*E*) gives the divisor for the calculation of grams of sugar per 100 reputed cc. from the specific gravity.

DEXTROSE.

A	B	C	D	E
0·9992	48·7130	1007·97	2·0675	3·855
1·0034	48·1702	1008·08	2·0999	3·848
1·9994	50·4500	1015·45	4·0243	3·839
3·0003	51·4028	1022·90	5·9705	3·836
4·0176	51·5618	1030·72	8·0311	3·825
4·9977	51·8332	1038·26	10·0108	3·822
5·9990	52·5148	1045·61	11·9444	3·819
7·0012	52·6845	1053·38	13·9984	3·813
7·9990	52·8802	1061·13	16·0513	3·808
9·0015	53·3225	1068·63	18·0398	3·804
9·9864	53·6794	1076·03	20·0182	3·798
1·0002	53·8410	1084·06	22·1483	3·795
1·9125	53·3030	1092·42	24·4141	3·786

LÆVULOSE.

A	B	C	D	E
1·1040	51·2864	1008·55	2·1710	3·938
2·0121	50·9296	1015·76	4·0130	3·927
3·0125	51·3828	1023·54	6·0008	3·923
4·0528	52·7696	1031·05	7·9186	3·921
3·9932	51·5144	1031·36	8·0047	3·918
5·0020	51·9567	1039·18	10·0044	3·916
5·9136	52·7690	1048·83	11·7202	3·910
6·9985	52·6476	1054·73	14·0207	3·904
8·2876	54·7342	1062·78	16·0922	3·901
8·9952	53·2702	1070·43	18·0753	3·896
10·0312	54·0708	1077·80	19·9949	3·890
11·0257	54·3534	1085·57	22·0211	3·886
11·6614	52·9094	1093·55	24·1021	3·881

MALTOSE.

A	B	C	D	E
0·9422	50·1806	1007·46	1·8916	3·944
1·9977	50·9160	1015·66	3·9850	3·930
3·1074	51·3990	1024·31	6·1926	3·926
3·8939	51·4710	1030·54	7·7963	3·917
5·0569	52·2945	1039·34	10·0504	3·914
5·9907	53·6860	1045·63	11·6680	3·911
7·0032	52·8330	1054·63	13·9795	3·908
7·9710	53·4580	1061·78	15·8319	3·902
8·0823	52·9998	1062·87	16·1081	3·903
8·9098	53·2972	1069·84	17·8847	3·905
8·9132	53·2600	1069·91	17·9052	3·904
10·0734	53·7766	1078·76	20·2073	3·898
10·9333	53·5393	1086·47	22·1869	3·897
11·7828	54·2558	1092·35	23·7227	3·893

Phosphoric Acid Manufacture: Rapid Works Method of ascertaining completion of Decomposition of Phosphate Rock by Sulphuric Acid.

By A. H. McDowell.

In the manufacture of phosphoric acid by digestion of phosphate rock with sulphuric acid, variations in the composition of the two raw materials render calculation of the proper relative proportion of each only approximately practicable.

The results desired is the maximum decomposition of rock with the minimum free sulphuric acid in the resulting phosphoric acid liquor. The determination of this balance by a titration with caustic alkali, even in the hands of a skilled chemist, is extremely uncertain and unsatisfactory. A volumetric sulphuric acid test, however, is sufficiently accurate for manufacturing purposes, and so simple that a workman of ordinary intelligence has no difficulty in understanding and manipulating it. This fact doubled the capacity of a certain phosphate of soda plant, for the foremen were able to test the liquor from the digestors and make the small necessary corrections. This enabled the plant to run continuously day and night.

The ground rock and sulphuric acid in the calculated amounts are digested in the usual manner for a sufficient time, say, four hours, before a sample is taken for test. The sample is filtered clear through a double filter paper and 50 c.c. diluted to 10° Bé. while hot are titrated with a standardized (10 per cent.) solution of barium chloride. The usual precautions for barium sulphate precipitation, boiling and the presence of hydrochloric acid, are taken, and at 2 c.c. intervals test portions are filtered off and tested with two or three drops of barium chloride solution, returning the test portion to the original solution under examination.

The sulphuric acid in the clear solution is present both free and combined as calcium sulphate. The calcium sulphate in solution under uniform manufacturing conditions is practically constant, and the amount of free sulphuric acid varies with the strength of

acid and the composition of the rock used. Experience shows that the best results are obtained when the test as outlined above requires the use of somewhere between 7 and 9 c.c. of barium chloride solution. A variation of not more than 2 c.c. from these limits should be corrected by the addition of a small amount of acid or rock to the digest. If the variation is greater than this another test is advisable.

Different methods of manufacture may cause a different amount of calcium sulphate to be in solution at the end of a digestion, thus changing the amount of barium chloride solution needed, but this can be adjusted to suit the special conditions. The daily control analysis of the mud and liquor will soon show what amount of barium chloride solution will correspond to satisfactory decomposition.

It has been found that a workman of ordinary intelligence can perform this test in about fifteen minutes.

Sur un Procédé de Séparation et de dosage du Zinc.

Par MM. P. Pipereaut et A. Vila,
Institut Pasteur, Paris.

Les diverses méthodes de séparation du zinc à l'état de sulfure donnent en général un précipité gélatineux, colloïdal dont la filtration et le lavage sont longs et difficiles. La méthode que nous allons indiquer, pour précipiter le sulfure de zinc, a l'avantage de donner dans un temps court un sulfure dense, facile à filtrer et à laver, ce qui rend des services appréciables dans les cas d'analyse où on désire un dosage rapide et sûr.

Emploi du soufre comme agent de précipitation.—Quand on fait une solution de zinc dans une lessive alcaline, soude ou potasse, et qu'on porte cette liqueur à l'ébullition, on voit, en ajoutant du soufre pur pulvérisé, la liqueur prendre tout d'abord une couleur jaune citron due à la solubilisation d'une partie du soufre. Bientôt apparaît un précipité de sulfure de zinc qui reste blanc si la soude est pure. Dès que le soufre ajouté est en excès le précipité prend une teinte rose indiquant par là que la quantité de soufre introduite est suffisante, et que tout le zinc est précipité de sa dissolution.

Les états du sulfure de zinc précipité.—Il y a quelques différences analytiques entre les divers précipités de sulfures que l'on peut obtenir par ce procédé, et suivant les conditions de dessiccation on observe de grandes variations dans les degrés d'hydratation.

Avec le sulfure blanc préparé à la température d'ébullition (105°) d'une lessive alcaline, à 20° B. environ, on obtient un produit dont la détermination de l'eau de constitution est très difficile.

Le tableau suivant le montre :

Sulfure de Zinc Blanc :	Zn %	S %	H_2O %
desséché dans le vide, $t = 18°$, pde Ct.	62·63	27·80	9·57
dans l'air, $t = 40°$ „	63·20	28·30	8·50
dans courant d'H, $t = 110°$	64·20	28·70	7·10
Calciné au rouge à l'abri de l'air ..	66·97	33·19	0·00

Tous ces corps, sauf le dernier, qui correspond à la blende, ne peuvent se rapprocher d'aucune des formules définies que l'on trouve dans les ouvrages ou travaux de la chimie du zinc.

Dans les mêmes conditions de préparation, le produit rose provenant de l'action d'un excès de soufre sur la liqueur de zincate de soude donne :

		Zn %	S %	H_2O %
Sulfure de Zinc Rose : (moyenne de deux analyses)				
sulfure séché à l'air, $t = 40°$	..	65·68	31·90	2·23

Ces produits hydratés calcinés, donnent à l'analyse les nombres de la blende.

On voit donc que ces substances ne sont pas de hydrates définis de sulfures mais que selon les circonstances de leur formation ils contiennent de quantités d'eau variables entre n H_2O et l'état anhydre.

On peut appliquer cette méthode de précipitation du zinc aux dosages et particulièrement dans les essais industriels où l'on désire faire vite et conserver cependant la précision.

Dans le cas complexe d'un minerai de zinc voici la technique que nous utilisons et qui nous a donné des résultats parfaitement concordants avec les méthodes classiques au sulfure de sodium, à l'hyposulfate de sodium (Riban).

Le minerai (5 gr.) finement pulvérisé est attaqué avec le mélange d'acides nitrique, chlorhydrique ; quand le minerai est désagrégé et qu'il ne reste plus de grains inattaqués, le résidu étant constitué par de la silice gélatineuse ou des fragments de quartz, on filtre et on lave le filtre. Les métaux lourds sont séparés de la liqueur acide et les liquides de la filtration sont reçus dans une fiole jaugée (250 cm.); on ajoute de la soude en quantité suffisante pour neutraliser l'acidité, précipiter puis redissoudre l'hydrate de zinc. On remplit alors la fiole jusqu'au trait de jauge. L'hydrate de fer et les autres corps insolubles qui peuvent se former sont filtrés sur un cône de porcelaine d'amiante de Garros.

On fait une prise de 50 c.c. de la solution limpide et on la met à bouillir dans un vase cônique de 500 c.c. en verre de Bohème. A la liqueur bouillante légèrement étendue d'eau distillée on ajoute 2 à 3 gr. de soufre en poudre fine.

La digestion du soufre commence aussitôt et la solution prend une teinte brun rouge. Après quelque temps d'ébullition du sulfure de zinc très dense se forme et l'ébullition devient tumultueuse. On règle l'opération en inclinant légèrement la fiole cônique sur la toile métallique de l'appareil de chauffage. La digestion du soufre terminée, on remplit au trois quarts la vase cônique avec de l'eau distillée bouillante et on laisse déposer. Après quinze minutes la

solution est prête à être décantée; on lave à l'eau chaude par décantation, puis on jette sur le filtre et on termine le lavage en faisant couler sur le précipité 300 à 500 cm. d'eau bouillante chargée de sulfhydrate d'ammonium. Le filtre et le précipité sont séchés puis grillés dans un moufle; l'atmosphère du moufle doit être parfaitement oxydante, ce qu'on réalise très bien avec les nouveaux brûleurs du type Meker.

L'oxydation du sulfure est terminée après trente à quarante minutes; on pèse l'oxyde et on peut s'assurer qu'il ne contient pas de sulfures, sulfates ou produits insolubles dans l'acide chlorhydrique.

Cette méthode convient parfaitement pour le dosage du zinc dans les matières premières et les produits employés dans l'industrie de la peinture, tels que les lithopones ou autres mélanges d'oxyde ou de sulfure de zinc avec des charges diverses.

Dans le cas d'une analyse de lithopone on ajoute à une prise de la substance (5 gr.) de l'eau et cinq à six c.c. de brôme, on agite à froid et on porte au bain de sable, enfin on termine l'attaque par addition d'acides azotique et chlorhydrique. On peut alors filtrer et laver le sulfate de baryum insoluble qu'on pèse, et faire un volume déterminé de la liqueur. Sur des volumes mesurés on détermine le soufre par les moyens connus et le zinc suivant les indications précédentes.

Determinazione volumetrica dell' Acido Selenioso.

Dr. Luigi Marino.

Il metodo proposto, è basato sull' ossidazione dell' acido selenioso con permanganato in soluzione alcalina. Dello metodo ha su gli altri il vantaggio di rendere indipendente la determinazione dell' acido selenioso dalle condizioni dell' esperienza, come concentrazione e temperatura, e di essere facilmente applicabile anche nel caso di seleniti insolubili. L' ossidazione dell' acido selenioso si fa vantaggiossamente con permanganato N/5. Dopo avvenuta la reazione si aggiunge acido ossalico N/5 in eccesso e poi si dosa questo di nuovo con permanganato.

I risultati sono buoni e l' errore massimo oscilla fra O. 16 e O. 20 per cento.

Si danno alcune applicazioni pratiche dell' anzidetto metodo.

An Essay upon Halogenimetry.

wo new processes for the separation and determination of Chlorine, Bromine, and Iodine.

By JUAN A. SANCHEZ.

The methods proposed are based on the facts that under certain definite conditions:—(1) by heating with sodium nitrate and sulphuric acid, the iodine can be completely expelled from a mixture of chlorides, bromides and iodides without any loss of hydrochloric or hydrobromic acid; (2) by distilling a mixture of chlorides and bromides with sulphuric acid and manganese dioxide, the whole of the bromine can be expelled without any liberation of chlorine.

Determination of iodine.—The total chlorine, bromine, and iodine in a mixture containing chlorides, bromides, and iodides is first determined by titration in the usual manner. Then 50 c.c. of a solution of the mixed salts, containing not more than 0·3 grm. of potassium iodide or its equivalent, are treated with 10 c.c. of a 20 per cent. solution of sodium nitrate and 5 c.c. of 20 per cent. (by vol.) sulphuric acid, and the mixture heated nearly to boiling, in a flask provided with a reflux tube, until the iodine is completely expelled. The residue is then again titrated to determine the unattacked chloride and bromide, and from the difference between the results of the two titrations, the proportion of iodine is calculated.

Determination of bromides in presence of chlorides.—60 c.c. of the solution of chloride and bromide, containing not more than the equivalent of 1 per cent. of sodium chloride, are mixed with 10 c.c. of 20 per cent. (by vol.) sulphuric acid and 5 grms. of manganese dioxide, and distilled for exactly five minutes (from the commencement of boiling) in a flask fitted with a tall vertical tube, which is bent twice at right angles, and then passes downwards through a condenser into a receiver containing 10—20 c.c. of a 50 per cent. solution of potassium iodide. The bromine distilled over liberates an equivalent quantity of iodine from the potassium iodide, and this is determined by titration with decinormal sodium thiosulphate. In the case of a mixture containing the three halogens, the iodine is first determined as described above, then 5 c.c. of 20 per cent. sulphuric acid and 5 grms. of manganese dioxide are added,

and the bromine determined. The chlorine is obtained by difference, the total of the three halogens being determined directly in a separate portion of the sample. In the case of mixtures of chlorides and bromides containing relatively large proportions of the former, the sample is first distilled with sulphuric acid and manganese dioxide as described above, and the distillation products (bromine and a small proportion of chlorine) are absorbed in a solution of alkali sulphite. The excess of alkali sulphite is then decomposed by heating with 20 per cent. sulphuric acid, and the bromine determined exactly by a fresh distillation, the proportion of chlorine being now too low to interfere.

Ueber die Frage der internationalen Regelung des Kali-Koeffizienten.

Von — PRECHT, *Neu-Stassfurt.*

Zur gewichtsanalytischen Bestimmung des Kalis wurde in früherer Zeit das Kali ausschliesslich mittels Platinchloridlösung als Kaliumplatinchlorid gefällt und nach dem Auswaschen und Trocknen gewogen. Aus dem Gewicht des Niederschlages wurde der Kaligehalt berechnet unter Zugrundelegung eines Atomgewichtes des Platins von 197,18. Die vor etwa 30 Jahren ausgeführte Atomgewichtsbestimmung von Seubert hat aber ergeben, dass die ältere Bestimmung des Atomgewichts nicht richtig ist, sondern dass das Atomgewicht des Platins 195 beträgt, und es wurde daher am 9. August 1892 im Verkaufssyndikat der Kaliwerke gelegentlich der Beratung über einheitliche Analysenmethoden in der Kaliindustrie darüber verhandelt, welche Atomgewichtszahl bei der Kalibestimmung zu Grunde gelegt werden soll. Bei diesen Verhandlungen war der Gesamtausschuss der Kaliwerke durch Herrn Oberbergrat Schreiber und Herrn Kommerzienrat Dr. Borsche, das Verkaufssyndikat der Kaliwerke durch Herrn Direktor Görz, Herrn Dr. Tietjens und Herrn Lierke vertreten. Ferner nahmen an den Verhandlungen 12 Vertreter der Kaliwerke des Verkaufssyndikats und der denselben zugehörigen chemischen Fabriken teil.

Bei diesen Verhandlungen wurde beschlossen, die alte Atomgewichtszahl des Platins von 197,18 beizubehalten und als

Faktoren zur Berechnung des Gehaltes an Chlorkalium, Kaliumsulfat und reinem Kali aus dem gefundenen Kaliumplatinchlorid, die Zahlen 0,3056 für KCl, 0,357 für K_2SO_4 und 0,1928 für K_2O festzusetzen. Dieses Festhalten an dem alten Atomgewicht wurde damit begründet, dass bei der praktischen Ausführung der Kalibestimmung niemals chemisch reines Kaliumplatinchlorid zur Wägung gelangte, sondern dass das Gewicht in der Regel durch Verunreinigungen und einen geringen Wassergehalt zu hoch ausfiele. Um diesen Fehler bei der Analyse auszugleichen, wurde nicht das durch die neue Untersuchung festgestellte richtige Atomgewicht von 195, welches schon an sich ein höheres Analysenresultat bedingte, sondern das frühere nicht mehr als richtig anerkannte Atomgewicht bei der Berechnung zu Grunde gelegt.

Bei der Untersuchung von Kaliumsulfat ist es bekanntlich nötig, die Schwefelsäure durch Chlorbarium auszufällen. Hierbei wird durch den Bariumsulfatniederschlag etwas Kali unlöslich niedergeschlagen, wodurch die Kalibestimmung zu niedrige Werte ergibt. Es wurde daher damals beschlossen, bei der Analyse des Kaliumsulfats zur Korrektion des vorstehend erwähnten Fehlers 0,3 % K_2SO_4 hinzuzurechnen.

Die Beschlüsse der Verhandlungen vom 9. August 1892, worüber ein gedruckter Bericht vorliegt, haben auch gegenwärtig in der Zusammenstellung der in der Kaliindustrie gebräuchlichen Untersuchungsmethoden noch Geltung behalten.

Ausser der damals allein als massgebend vereinbarten Bestimmung des Kalis mittels Platinchlorid ist aber später die Kalibestimmung mittels Ueberchlorsäure mehr und mehr in Aufnahme gekommen. Auf dem internationalen Kongress für angewandte Chemie in Berlin 1903 habe ich in einer gemeinsamen Sitzung der Sektion für Agrikulturchemie und der Sektion für analytische Chemie die Vorteile der Ueberchlorsäuremethode hervorgehoben, und infolgedessen ist sie allgemein zur Anwendung gekommen und bei den meisten landwirtschaftlichen Versuchsstationen eingeführt. Bei der Ueberchlorsäuremethode fällt die internationale Regelung des Kali-Koeffizienten fort, da man mit dem Atomgewicht des Platins nicht mehr zu rechnen hat und nur die genau festgesetzten Atomgewichte des Kaliums, Chlors und Sauerstoffes in Frage kommen. Das zur Wägung gelangende Kaliumperchlorat ist vollständig rein und leicht zu trocknen, sodass bei der Ueberchlorsäuremethode eine Fehlerquelle, wie bei der Platinmethode,

nicht vorhanden ist. Die internationale Regelung des Kali-Koeffizienten hat daher gegenwärtig nur noch Bedeutung, wenn man die jetzt allgemein gebräuchliche Kalibestimmung mittels Ueberchlorsäure durch die ältere Bestimmungsmethode mittels Platinchlorid kontrollieren will, z. B. bei Schiedsanalysen. Derartige Kontrolluntersuchungen dürften aber nur noch selten notwendig werden, da die Ueberchlorsäuremethode zur Zeit so sorgfältig durchgearbeitet ist, dass bei vorschriftsmässigem Arbeiten ein einwandfreies und zuverlässiges Resultat garantiert werden kann.

Von Seiten des Kalisyndikats liegt keine Veranlassung vor, Aenderungen in den Vorschriften der Untersuchungsmethoden für Kalisalze vorzunehmen, da erfahrungsgemäss beim Arbeiten nach den gegenwärtigen Vorschriften richtige Resultate erzielt werden. Wenn aber von der internationalen Kommission für die Analysen der Kunstdünger und Futtermittel darauf gedrungen wird, den Kali-Koeffizienten bei der Kaliuntersuchung mittels Platinchlorid international festzulegen, so bin ich der Ansicht, dass man die althergebrachte Vorschrift, an der man für ewige Zeiten doch nicht festhalten kann, fallen lassen und das wissenschaftlich genau festgestellte neuere Atomgewicht von 195,0 der internationalen Atomgewichtstabelle von 1909 zu Grunde legen müsste. Der Koeffizient für Chlorkalium würde dann nicht mehr 0,3056, sondern 0,30686 betragen und die Resultate der Kalibestimmung würden dadurch höher ausfallen als bisher. Es müsste dann aber gleichzeitig als Korrektion ein Abzug von den erhaltenen Resultaten vereinbart werden, um nicht den Vorwurf aufkommen zu lassen, dass man die Abnehmer durch zu hohe Analysenbefunde übervorteilen wollte. Für hochprozentiges Chlorkalium würde die Korrektion etwa 0,3 bis 0,4% betragen. Bei der Untersuchung von Kaliumsulfat würde dieser Abzug von dem gefundenen Resultat nicht notwendig sein; man brauchte nur von der bisher vorgenommenen Erhöhung des Resultats um 0,3 % abzusehen.

Bei der Untersuchung von niedrigprozentigen Düngesalzen bezw. Kalirohsalzen ist nur eine sehr geringe Korrektion vorzunehmen, die zweckmässig noch einmal durch mehrfache Versuche festzustellen sein würde, da künftighin die Platinchloridmethode wohl nur noch dann zur Anwendung kommt, wenn es sich um Kontrolluntersuchungen handelt, und daher möchte ich die Frage unentschieden lassen, ob und in welcher Höhe die Korrektion bei den Unter-

suchungen von Kalirohsalzen vorzunehmen ist, wenn man mit reinem Platinchlorid arbeitet.

Die vorstehenden Erörterungen möchte ich folgendermassen zusammenfassen:

"Bei einer internationalen Regelung des Kali-Koeffizienten ist das richtige Atomgewicht des Platins von 195,0 zu Grunde zu legen und es sind alle diejenigen Korrektionen vorzuschreiben, welche bei den verschiedenen Marken zur Erzielung eines möglichst richtigen Befundes notwendig sind; für Kaliumsulfat wäre die jetzt gebräuchliche Korrektion fallen zu lassen."

Bibliography of the Progress in Analytical Separation of the Less Common Elements, 1907–9.

Cerium, Glucinum, Gold, Indium, Iridium, Lithium, Molybdenum, Palladium, Platinum, Selenium, Tantalum, Tellurium, Thorium, Titanium, Tungsten, Uranium, Vanadium, Zirconium.

By Herbert R. Moody, Ph.D., *College of the City of New York.*

Cerium.

Determination of Ceria in Rocks.

Ber. 41, p. 4373. The precipitation is effected as oxalate with the subsequent separation of calcium and cerium.

The estimation of Cerium in the presence of Th, Y, La, Di, Zr, etc.

Am. J. Sci., 26, p. 83. The process depends upon the oxidation of cerous to ceric salts by potassium ferri-cyanide and the determination of the potassium ferro-cyanide thus formed.

Glucinium (*Beryllium*).

Estimation of Beryllium.

J. Am. Chem. Soc., 28. This separation is based upon the solubility of beryllium hydroxide in an excess of $NaHCO_3$ and the complete insolubility of the hydroxides of iron and aluminium.

Separation of Beryllium from Aluminium.

Ber. 39, p. 3366, and Ber. 39, p. 3868. Slightly acid solutions with $Na_2S_2O_3$ have all aluminium precipitated as hydroxide while beryllium remains in solution.

Quantitative determination of Beryllium.

Ber. 39, p. 3368. Beryllium hydroxide is formed by the addition of potassium iodide and iodate solutions in neutral or weakly acid solution.

Gold.

Recognition of Gold by Microcosmic Bead.

Zeit. Chem. und Ind. Kolloide, 2, p. 273. Gold imparts a blue coloration. Test is delicate to 30 millionths of a milligram.

The recovery of Gold Residues.

Pharm. Zeit. 52, p. 168. Precipitation with $FeSO_4$ in alkaline solution.

Determination of Gold by Electric Conductivity Measurements.

Monatsch. f. Chem. 27, p. 59.

Determination of Gold.

Z. Anal. Chem. 45, p. 87. Gold is precipitated by sheet nickel.

Colorimetric determination of small quantities of Gold.

Z. Anorg. Chem. 49, p. 172. Red colour is developed in a neutral solution by an aqueous solution of acetylene.

Detection of Gold.

Z. Anal. Chem. 25, p. 342.

Electrolytic Precipitation of Gold.

J. Am. Chem. Soc. 28, p. 1350. Conditions given for best results in cyanide solutions.

Determination of Gold by Sucrose or Dextrose.

Zeit. Chem. u. Ind. der Kolloide 2, p. 103. The precipitated metallic gold is filtered off in a Gooch crucible.

Reaction between Gold Chloride and Formaldehyde.

Z. Chem. und Ind. der Kolloide. Precipitation is incomplete without a sufficient amount of NaOH present.

Indium.

The separation of Indium and Iron.

J. Am. Chem. Soc. 30, p. 209. The iron is precipitated by nitroso-β-naphthol in 50 per cent. acetic acid.

Iridium.

The use of Iridium Crucibles.

Proc. Roy. Soc. 80, p. 541. These are compared favourably with those of platinum.

Detection of Iridium in Commercial Platinum.

Comptes Rend. 142, p. 631. Iridioplatinum is treated with sulphuric acid, on heating with ammonium salts iridium is shown by a green solution which turns violet when boiled with nitric acid.

Lithium.

Separation of Lithium Chloride from Chlorides of other Alkalies and from the Chloride of Barium.

J. Am. Chem. Soc. 30, p. 1104. In anhydrous pyridine the alkali chlorides (except LiCl) and $BaCl_2$ are insoluble. LiCl is extracted, converted to Li_2SO_4 and weighed.

Molybdenum.

Use of Zinc Reductor for Molybdic Acid.

Am. Jour. Sci. 24 (1907), p. 313. Use of oxidizing agent in excess in the receiver. Good results were obtained.

Determination of Molybdenum in Wulfenite.

West. Chem. Met. 3 (Dec., 1907), p. 218. Involves removal of Pb, Fe, etc., solution of molybdenum sulphide in Br and subsequent gravimetric determination as lead molybdate or volumetric determination by titration with lead acetate and tannic acid indicator.

The Determination of MoO_3 in presence of Vanadic acid.

Am. J: Sci. 25, p. 332. Good results were obtained.

Use of Ammonium Molybdate for Nickel tests.

Bull. Soc. Chem. (4) 3-4, pp. 775 and 894.

Estimation of Molybdenum in the presence of Tungsten, Chromium, Nickel and Vanadium.

Stahl u. Eisen 28 p. 853. Molybdenum is finally precipitated as lead molybdate.

Estimation of Molybdenum in Steel (in presence of Vanadium, Chromium and Nickel).

J. Am. Chem. Soc. 30, p. 1229. Molybdenum is precipitated as sulphide in presence of the iron, in sulphuric acid solution.

A Rapid Volumetric Method for Molybdenum.

Eng. and Min. Journ. 82, p. 818. The titration is done with lead acetate, after an oxidizing fusion.

The Reduction of Molybdic Acid by Metallic Molybdenum preparatory to Titration with Potassium Permanganate.

Compt. Rend. 143, p. 744.

Phosphormolybdic acid as a reagent for Potassium.

Chem. Zeit. 30, pp. 1299 and 32, pp. 1125 and 1138. Potassium gives a yellow precipitate while calcium and magnesium give none.

Qualitative Colour Test for Molybdenum.

Chem. News 97, p. 40. H_2O_2 in an ammoniacal solution gives intense brown colour due to per-molybdate.

Variation in the composition of Ammonium Phospho-molybdate formed in Phosphorus Determinations.

Compt. Rend. 146, p. 758.

Palladium.

Separation of Palladium from Other Members of the Platinum Group.

Chem. Zeit. 30, p. 714. Palladium is precipitated with freshly made silver iodide which reacts only with palladium chloride.

Determination of Palladium by Electrical Conductivity Methods.

Monatsch. f. Chem. 27, p. 59. The increase in conductivity is directly proportional to the amount of palladium present.

Use of Palladium as a Substitute for Platinum in Elementary Analysis.

Ber. 40, p. 3217, and Ber. 40, 3677.

Separation and Determination of Palladium by Acetylene.

Z. Anal. Chem. 46, pp. 141 and 46, p. 145. Palladium is quantitatively precipitated as a red-brown precipitate, *not* of constant composition.

Platinum.

Deterioration of Platinum Vessels.

Zeit. Angew. Chem. 20, p. 1892. Recommended to heat electrically rather than with gas.

Platinum Alloys—Detection of Ruthenium in.

Chem. Ztg. 3, p. 77.

Use of Platinum Chloride for Estimating Potassium.

Chem. Zentr., 1908, II., 1647. Discussions of discrepancies.

Recognition of Platinum by Microcosmic Bead.

Z. Chem. und Ind. Kolloide. 2, p. 273. Reddish colour formed, delicate for ·00008 mg. interfered with only by large excess of gold.

The Separation of K and Na as Chlorplatinates.

Bull. Acad. Sci., Cracovie, 1906, p. 796.

Recovery of Platinum Residues.

Pharm. Ztg. 52, p. 168. Platinum precipitated with NH_4Cl, mixed with oxalic acid and strongly heated.

Action of Sulphuric Acid on Platinum Salts.

Compt. rend. 142, p. 631.

Detection of Platinum.

Zeit. Anal. Chem. 25, p. 342.

Selenium.

Assay of Bullion containing Selenium.

Eng. Min. Journ. 82, p. 1057.

Thiocyanselenious Acid and the Determination of Selenium.

Chem. Ztg. 32, p. 468. This allows of separation from tellurium which forms no corresponding compound.

Microchemical detection of Selenium in Copper.

Oestr. Z. Berg- u. Hüttenw. 55, p. 473. Orange-red cadmium selenide is the form in which identification is made.

Tantalum.

Estimation of Tantalum and Niobium in the presence of Titanium.

Am. J. Sci. 22, p. 520.

Tellurium.

The Gravimetric Determination of Tellurium.

J. Am. Chem. Soc. 30, p. 387. This is a comparison of the various methods of precipitation, including precipitation by the simultaneous use of SO_2 and N_2H_42HCl.

The Assay of Telluride Ores.

J. Am. Chem. Soc. 30, p. 1023. A series of tests lead the author to the conclusion that tellurium as a cause of irregularity in crucible work has been over-estimated.

Behaviour of Tellurium in Assaying.

Trans. Inst. Min. and Met., May, 1909. Directions are given to avoid loss of precious metals in the assay of telluride ores.

Thorium.

Separation of Titanium from Zirconium and Thorium.

Z. Anorg. Chem. 56, p. 344.

Separation of Thorium, Titanium and Zirconium from Iron.

Z. Anorg. Chem. 56, p. 348.

Titanium.

Volumetric Determination of Titanium.

Chem. Ztg. 61 (59), p. 738. This involves reduction with zinc and titration with ferrous sulphate. Another modification employs reduction by Zn-Mg and titration for the ferric chloride, KSCN for an indicator.

Volumetric Determination of Titanium.

Am. J. Sci. 25, p. 130. This involves oxidation of titanium sesquisulphate to disulphate by $Fe_2(SO_4)_3$. The reduced iron is then determined by $KMnO_4$.

Use of Titanium Tri-chloride as a Reducing Agent in Volumetric Work such as Iron Determination and Sodium Hydrosulphite.

Ber. 40, p. 3819. A continuation of an earlier paper, Ber. 36, p. 1549.

Quantitative separation of Titanium from Iron.

Atti. Acad. Lincei (5) 16, (1), p. 331. This involves fusion with $KHSO_4$ and treatment with H_2SO_4 previous to solution in water: Iron is removed electrolytically. The titanium is precipitated by NH_4Cl and NH_4OH and the co-precipitated Al dissolved out by excess of NaOH.

Volumetric Determination of Titanium.

Zeit. Anorg. Chem. 57, p. 278.

Qualitative Determination of Titanium by Dihydroxymaleic Acid.

Proc. Chem. Soc. 24, p. 133.

The Estimation of Titanium.

Chem. Eng. 7, p. 198.

Titanous Chloride Used for the Volumetric Determination of Iron or Chromium in the Presence of Each Other.

J. Soc. Chem. Ind. 27, p. 673.

Titanium tri-Chloride used for the Volumetric Estimation of Copper.

Pr. Chem. Soc. 22, p. 244. This is based upon the discharge by

the titanium chloride of the colour of cupric sulphocyanate when iron salts are present.

Separation of Ti in presence of Niobium and Tantalum.

Am. J. Sci. 22, p. 520.

The Colorimetric Determination of Titanium.

Chem. Ztg. 31, p. 263. This method is based on the yellow colour produced by H_2O_2. The $KHSO_4$ fusion is dissolved in sulphuric acid to prevent formation of basic sulphate.

Another Colorimetric Determination of Titanium.

J. Am. Soc. 29, p. 481. This method involves fusion with alkali peroxides.

Separation of Titanium from Zirconium and Thorium.

Zeit. Anorg. Chem. 56, p. 344. This is based upon the precipitation of ammonium Zirconium (or Thorium) salicylate while the basic titanium salicylate remains in solution.

Use of Titanium Sesquisulphate to precipitate Copper.

Ber. 41, p. 498.

Determination of Titanium in Ferro-titanium.

Eng. and Min. J. 85, p. 1200. Iron is removed by H_2S after NH_4OH and tartaric acid have been added and then titanium precipitated with ammonia after removing tartaric acid by HNO_3.

Determination of Iron in the Presence of Titanium.

Zeit. Anorg. Chem. 54, p. 213. The Iron and Titanium are simultaneously reduced, then the titanium re-oxidized by cupric sulphate. The iron is afterwards determined by $KMnO_4$.

TUNGSTEN.

Determination of Tungsten, Chromium and Silicon in Chrome-tungsten Steel.

Stahl u. Eisen 28, p. 1819. Tungsten precipitated as WO_3 by HNO_3 leaving Chromium and iron in solution.

Separation of Tungstic acid and Silica.

Compt. Rend. 147, p. 795. The mixed WO_3 and SiO_2 is treated with the vapours of chloroform at 500° converting WO_3 to oxychloride.

Determination of Tungstic Acid in Ores and Concentrates.

Chem. Eng. 5, p. 27. Involves separation of WO_3 and SiO_2 by solution in NH_4OH and NH_4Cl.

Phosphotungstic Acid as a Re-agent for Potassium. Used as Sodium Phosphotungstate.

Chem. Ztg. 31, p. 158.

Separation of Tungsten and Tin.

Zeit. Angew. Chem. 19, p. 473. Separated in oxide form by reducing the tin with zinc and dissolving away the tin with HCl. Subsequent oxidation insures that all tungsten is in oxide form.

Alkalimetric Determination of Tungsten in Steel.

J. Am. Chem. Soc. 29, p. 477. This involves the conversion of tungstic oxide to sodium tungstate by standard NaOH in excess, using HCl and phenolphthalein indicator to titrate back the excess of NaOH.

Separation of Tungstic Acid from Phosphoric Acid.

Zeit. Anal. Chem. 47, p. 37. The tungsten is precipitated as benzidine tungstate by benzidine chloride in excess.

The Estimation and Separation of Tungstic Acid.

Compt. Rend. 146, p. 1102. Through use of a mixture of Cl and sulphur chloride, volatile oxy-chlorides form and are given off and finally converted to WO_3 and weighed.

The Separation of Silica and WO_3.

Compt. Rend. 146, p. 1319. Mixture heated in current of hydrogen till reduction is finished. WO_3 becomes partly lower oxides, partly metal. Dry Chlorine is then passed through producing WCl_6 and $WOCl_4$, which pass over.

Van Knorr's Method for the Separation of Tungsten from Chromium.

Zeit. Anal. Chem. 47, p. 337. This involves the use of benzidine chloride as a precipitant.

Determination of Tungsten in Steel.

Zeit. Anorg. Chem. 59, p. 183. Modification of von Knorre's benzidine method necessitated by the presence of Cr.

Estimation of Tungsten in Presence of Chromium, Niobium, Molybdenum and Uranium.

Stahl u. Eisen 28, p. 853. Tungsten is precipitated as WO_3.

Sodium Phosphotungstate as a Qualitative Re-agent for Ferrous Iron.

J. Pharm. Chem. 29, p. 238. Deep blue colour denotes presence of iron.

Determination of Tunstic Acid in Ores.

Min. Jour., Feb. 22, 1908. Process involves solution in standard solution of ethylamine and determining excess of latter by titrating with oxalic acid.

Uranium.

Determination of Uranium.

J. Am. Chem. Soc. 28, p. 1443. This process depends upon the solubility of Uranium carbonate in excess of Na_2Co_3 and the subsequent precipitation by $(NH_4)_2HPO_4$.

Use of Uranium Compounds for the Titration of Phosphoric Acid.

Mon. Sci. (4) 21 (II.), p. 753.

Differential Reaction for Uranium and Cadmium. This involves formation of a yellow precipitate when alkaline solution of thiosinamine is used. Not produced by other metals.

Solubility of Rare Earth Oxalates in Uranyl salts.

Z. Anal. Chem. 47, p. 677.

Determination of Uranium and Vanadium.

J. Am. Chem. Soc. 28, p. 1443. This method involves precipitation of the uranium as ammonium-uranyl phosphate.

Separation of Uranium and Vanadium.

Eng. and Min. Journal 87, p. 155. The uranium is precipitated as ammonium-uranyl phosphate. Minute directions are given for the process.

Vanadium.

Technical Analysis of Iron Vanadate.

Electrochem. and Met. Ind. 5, p. 495. Iron and Silicon being removed the vanadium is determined in the filtrate by standard $KMnO_4$.

Estimation of Vanadium when it is together with Tungsten, Chromium, Nickel and Vanadium.

Stahl u. Eisen 28, p. 853. The vanadium is either precipitated as manganese vanadate or titrated with $KMnO_4$.

Estimation of Vanadic Acid by $SnCl_2$.

Am. Chem. Anal. 13, p. 209, and Bull. Soc. Chem. 3-4, p. 326. Ammonium molybdate is used as the indicator. $SnCl_2$ is a 2-3 per cent. solution.

The reduction of Vanadic acid by Zinc and Manganese.

Am. J. Sci. 25, p. 233, and Chem. News 98, p. 2. V_2O_2 and V_2O_3 form. Reduced solution cannot be titrated in open air. Jones reductor with ferric alum in receiver overcame this difficulty.

The determination of Vanadic Acid in the Presence of Molybdic Acid.

Am. J. Sci. 25, p. 332.

The Determination of Vanadium.

Eng. Min. Journ. 85, p. 962. Iron is removed. Vanadium is reduced by SO_2 and titrated with $KMnO_4$.

Extraction of Iron and Vanadium in Presence of Each Other.

Am. J. Sci. 26, p. 79. This avoids the slow separation of Fe and V. Vanadium is reduced to V_2O_4 with SO_2 and titrated with $KMnO_4$. After titration vanadium is reduced to V_2O_2 in a Jones reductor. The difference in the two titrations affords necessary data.

Determination of Vanadium, Molybdenum, Chromium and Niobium in Steel.

J. Am. Chem. Soc. 30, p. 1229.

Determination of Vanadic and Chromic Acids in the Presence of Each Other.

Am. J. Sci. 26, p. 333. The process involves noting the differential reducing action of HBr and HI. HBr reduces Vanadic acid to V_2O_4. HI reduces V_2O_4 to V_2O_3.

Am. J. Sci. 27, p. 174. Additional data as above.

Determination of Vanadium and Uranium.

J. Am. Chem. Soc. 28, p. 1443, and Eng. and Min. J. 87, p. 155. The two metals are dissolved away from others by solution in excess of Na_2CO_3. The uranium is then precipitated by $(NH_4)_2 \cdot HPO_4$ and the vanadium reduced and titrated with $KMnO_4$.

Zirconium.

Separation of Titanium from Zirconium and Thorium.

Zeit. Anorg. Chem. 56, p. 344. This involves the precipitation with ammonium salicylate. Basic titanium salicylate is completely soluble in hot water, while zirconium remains quantitatively precipitated as ammonium-zirconium salicylate.

La difenilcarbazide simmetrica nei metodi volumetrici per precipitazione.

Nota di BERNARDO ODDO.[*]
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Qualche anno fa[†] ho mostrato che si riesce a dosare direttamente il rame nei suoi sali con una soluzione titolata di xantogenato di potassio $CS\langle^{OC_2H_5}_{SK}$ impiegando come indicatore la difenilcarbazide simmetrica:

$$OC\langle^{NH\cdot NH\cdot C_6H_5}_{NH\cdot NH\cdot C_6H_5}$$

Questa sostanza venendo a contatto coi sali di rame forma secondo Cazeneuve[‡], un difenilcarbazone ramoso

$$OC\langle^{NCu\cdot NCu\cdot C_6H_5}_{N=N\cdot C_6H_5}$$

il quale ha la proprietà di colorare la soluzione così intensamente in violetto da permettere di rintracciare il rame persino alla diluizione di 1/100,000 che non viene svelato dal ferrocianuro di potassio.

Ho notato infatti allora che aggiungiendo ad una soluzione di un sale di rame un poco di difenilcarbazide e poi la soluzione ecquivalente di xantogenato di potassio, metre si forma il precipitato giallo di xantogenato rameoso, la colorazione violetta intensa del carbazone rimane finchè non ci sia aggiunta la quantità teorica del reattivo e sparisce subito appena se n'è aggiunto un piccolo eccesso.

Nell' intento di estendere l'impiego di questo importante reattivo al dosaggio volumetrico di altri metalli, ho rivolto la mia attenzione ai sali di mercurio e di piombo, perchè anche con i primi la difenilcarbazide dà un difenilcarbazone mercuroso

$$OC\langle^{NHg\text{-}NHg\cdot C_6H_5}_{N=N\cdot C_6H_5}$$

d'una tinta bleu egualmente intensa e differente da quella dei sali di rame; e si ha inoltre la particolarità che la colorazione bleu

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* Vedi Gazz. Chim. ital. 1909, 39, I pag. 667 e 671; Journal of the Society of Chemical Industry, 1909, pag. 913 e 918.

† Rend. Acc. Lincei 12, 1,435 (1903); Gazz. Chim. it. 33, II., 134 (1903); Guareschi, Nuova enciclop. di chim. Vol. II., p. 397 (1906).

‡ Bull. Soc. chim. de Paris, 23, p. 592 e 701 (1900).

carica presenta una certa stabilità all' azione dell' acido nitrico. Così 10 cc. di una soluzione di sale di mercurio, sia al minimo che al massimo della concentrazione dell' 1/10,000, agitati con 5 cc. di una soluzione benzenica, satura a freddo, di difenilcarbazide dà ancora una colorazione bleu assai intensa, ed una goccia di acido nitrico concentrato non arriva a distruggerla.*

Questa condizione mi ha reso quindi possibile la titolazione del mercurio in diversi campioni di nitrato mercuroso, che devono essere necessariamente, come è noto, acide per acido nitrico, e in questa nota per ciò che riguarda i sali di mercurio, descrivo solamente l' applicazione del metodo al dosaggio del mercurio nei suoi sali al minimo precipitandolo come cloruro mercuroso.

I sali di piombo, con la difenilcarbazide non dànno che una tinta leggermente rosa e perchè si ottenga si richiedono delle condizioni speciali e delle soluzioni di media concentrazione. Sono riuscito però egualmente a dosare il piombo, mediante lo stesso indicatore, impiegando come reattivo precipitante una soluzione titolata di cromato di potassio.

La difenilcarbazide è anche per l' acido cromico un reattivo di una sensibilità che supera non solo quella data dalla decomposizione dell' ioduro di potassio, ma anche dalla formazione dell' acido percromico bleu, a contatto dell' acqua ossigenata, che pure permette di svelare l' acido cromico in una soluzione all' 1/10.000.

Ma mentre una soluzione all' 1/100.000 non dà più la formazione dell' acido percromico, una magnifica tinta violetta si ottiene addizionando di difenilcarbazide in polvere la soluzione del cromato acidificata con acido acetico o meglio con acido cloridrico, e ciò anche per soluzione all' 1/1000.000.*

L'esattezza nel metodo di dosaggio volumetrico del piombo mi ha consigliato inoltre di dosare anche l' ione SO_4'', facendo uso di due soluzioni fra loro equivalenti di $Pb(NO_3)_2$ e di K_2CrO_4, ed anche in questo caso i risultati sono stati ottimi. Volendo invece applicare lo stesso metodo al cromato per il dosaggio del bario, non sono riuscito finora ad ottenere dei risultati positivi, quantunque la

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* Cazeneuve, l. c. Meyer, Jahrbuch d. Chemie 10, 54 (1900). Bull. Soc. Chim. de Paris, 25, pag. 758 e 761 (1901); Meyer, Jahrbuch d. Chemie, 11, 438 (1901).

* Quando io aveva già impiegato la difenilcarbazide per il dosaggio volumetrico del rame, L. Brandt, tre anni dopo (Zeit. ana. Ch. t. 45, p. 96 (1906) l'applicò anche alla titolazione del ferro per mezzo del bicromato potassico, per quanto nella mia citata memoria mi sia riservato di estendere l'uso di questo indicatore per il dosaggio volumetrico di altri metalli.

difficoltà non consista che nello stabilire alcune modalità nella precipitazione di questo metallo allo stato di cromato.

Preparazione dell' indicatore. La difenilcarbazide, che si ottiene facilmente, come ho fatto notare altrove,* facendo agire alla temperatura di non più di 150° a bagno di olio una molecola d'urea con due molecole di fenilidrazina fino a che cessa la sviluppo di ammoniaca, venne da me usata in tutti i casi in soluzione acetica, e di questa ho preparato delle cartine, impiegando, così il metodo alla tocca.

Questo metodo, certamente, in molti casi conduce ad una perdita di tempo non indifferente; ma nel caso del mercurio, data la facilità con cui si deposita il cloruro mercuroso, appena formatosi, l' operazione viene eseguita in pochi minuti. Aggiungere la difenilcarbazide al liquido da precipitare non è consigliabile perchè si formano dei passaggi graduali di colorazione che rendono difficile stabilire la fine della reazione.

Anche il cromato di piombo non tarda molto a depositarsi, per quanto sia sempre bene, come farò meglio notare in seguito, di fare in questo caso i prelevamenti del liquido dopo alcuni minuti che si è aggiunto il cromato alcalino.

Per potere ottenere delle cartine alla fenilcarbazide quasi del tutto incolore e che si conservino inalterate per lungo tempo tenendole in vasetto colorato ed a tappo smerigliato, io consiglio di fare dei piccoli nastri di carta bibula e di immergerli nella soluzione della carbazide in acido acetico glaciale. Avvenuto l'assorbimento si spremono per bene tra carta bibula e poi si fanno asciugare rapidamente, introducendole in una stufa riscaldata fra i 60 e i 70°.

1°—*Dosaggio del mercurio nei suoi sali al minimo.*—I metodi proposti per la determinazione volumetrica del mercurio sono abbastanza numerosi, ma fra i tanti solo due vengono comunemente usati e consigliati dai trattatisti.† Sono basati sull' insolubilità del cloruro mercuroso che si forma per aggiunta di un cloruro solubile sui sali solubili di mercurio al minimo.

Nella soluzione fredda del sale mercuroso si versa una soluzione normale decimo di cloruro di sodio, fino a che non si forma più precipitato; poi se ne versa un leggero eccesso, si filtra, si lava e si determina l' eccesso del cloruro con una soluzione equivalente di

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* L. c.

† Fresenius: Traité d'analyse chimique quantitative, 8va dition française, par Gautier, 1909.

nitrato di argento, usando come indicatore il cromato neutro di potassio.

Secondo Hempel* invece dopo avere precipitato il sale mercuroso con cloruro sodico e filtrato e lavato il cloruro formatosi, si tratta questo con ioduro di potassio e con una soluzione titolata di iodio: avviene allora la reazione:

$$Hg_2Cl_2 + 6\ KI + 2I = 2HgK_2I_4 + 2\ KCl$$

per cui basta trattare in seguito con una soluzione equivalente d' iposolfito di sodio fino a scomparsa della tinta bruna dovuta all' eccesso di iodio e titolare su una parte aliquota l' eccesso di iposolfito con una soluzione equivalente di iodio per arrivare al quantitativo di mercurio.

Sia l' uno che l' altro metodo dànno risultati soddisfacenti; ma ambedue oltre a richiedere filtrazioni e lavaggi, richiedono anche la preparazione di due soluzioni titolate, che, data la loro natura, eccezione fatta di quella di cloruro di sodio, bisogna averle preparate di recente.

Impiegando invece la difenilcarbazide come indicatore oltre ad avere dei buoni risultati, l' operazione viene eseguita in pochi minuti e non si richiede che una soluzione titolata di cloruro di sodio. Per l' esattezza del metodo farò poi quì notare che bisogna aver cura di fare il saggio con una goccia di liquido limpido, perchè il cloruro mercuroso, se umido, reagisce anch' esso con la difenilcarbazide.

Soluzioni Titolate.

(1°) *Soluzione di cloruro sodico.*—Feci uso di soluzione normale decimo di cloruro di sodio cristallizzato, puro; il liquido venne controllato con analisi ponderale.

(2°) *Soluzione di nitrato mercuroso.*—Ho usato diversi campioni di nitrato mercuroso della casa Kahlbaum e di tutti ho ottenuto risultati ottimi che controllavo volta per volta mediante dosaggi ponderali:—

1° cc. 27,90 di $HgNO_3$, corrispondenti a gr. 0,6054 di Hg, richiesero cc. 29,88 di Na Cl $\frac{N}{10}$

2° cc. 20,00 di $HgNO_3$, corrispondenti a gr. 0,4340 di Hg richiesero cc. 21,20 di Na Cl $\frac{N}{10}$

	I.	II.	Calcolato
Hg	gr. 2,13	gr. 2,11	2,17

* Ann. der Chemie und Pharm. cx., 176.

L'operazione viene eseguita nel seguente modo:

Alla soluzione di nitrato mercuroso convenientemente diluita e neutralizzata della maggior parte di acido nitrico libero con carbonato sodico si aggiunge a piccole riprese la soluzione normale decimo di cloruro sodico. Si ritiene completa la precipitazione quando una goccia di liquido limpido sovrastante il precipitato di cloruro mercuroso non impartisca più alcuna colorazione alla cartina alla difenilcarbazide.

Raggiunto questo punto una goccia di soluzione di sale mercuroso aggiunta al liquido dove è avvenuta la precipitazione, fa si che si ottiene per un successivo saggio alla tocca una sensibile colorazione celeste pallida, che scompare a sua volta per aggiunta di una goccia di soluzione di cloruro sodico.

Il mio metodo si presta inoltre per il dosaggio del mercurio nei suoi sali al minimo anche in presenza di sali mercurici. Basta a tal uopo infatti precipitare con un eccesso di soluzione titolata di cloruro sodico il mercurio al minimo, filtrare, precipitare il sale mercurico con idrogeno solforato, filtrare di nuovo e titolare infine (dopo avere eliminato per evaporazione, tutto l'idrogeno solforato) con una soluzione di nitrato mercuroso a titolo noto, l'eccesso di cloruro sodico perchè si abbia il quantitativo di mercurio al minimo.

2°—*Dosaggio del piombo.*—(*) Il metodo che propongo è fondamentalmente lo stesso di quello proposto da Schwarz† e consiste nel precipitare il piombo alla stato di cromato mediante una soluzione titolata di cromato neutro di potassio.

Mentre però riesce difficile di fissare esattamente la fine della precipitazione, usando, come fa Schwarz come indicatore il nitrato di argento, impiegando le cartine all' acetato di difenilcarbazide, si ottengono delle indicazioni precise della fine della reazione.

Soluzioni Titolate.

(1°) *Soluzione di piombo.*—Ho usato soluzioni normali decimo di nitrato di piombo, che ho controllato con dosaggi ponderali.

(2°) *Soluzione di cromati.* Mi sono servito di soluzioni decinormali sia di cromato potassico che di bicromato ed ho ottenuto sempre dei risultati molto soddisfacenti superiori a quelli che si ottengono impiegando il metodo alla tocca con nitrato d'argento.

* Le esperienze relative a questo dosaggio e quelle per la determinazione dell' acido solforico vennero fatte in collaborazione col Dr. A. Beretta.

† Dingl. polyt. Journal, clxix., 284; Fresenius, L. c. pag. 357.

Secondo qualche autore* la comparsa della colorazione rossa, dovuta alla formazione di cromato d' argento, avviene assai prima che si completi la precipitazione del piombo; essa va sensibilmente aumentando man mano che per successive aggiunte di bicromato potassico diminuisce nel liquido la quantità di piombo disciolta ed acquista infine una intensità molto più grande quando il piombo sia stato completamente precipitato.

Ho voluto verificare quest' asserzione e sono arrivato a conclusioni opposte: perchè si possa stabilire la fine della reazione, impiegando come indicatore il nitrato di argento, è necessario aggiungere un eccesso di bicromato alcalino che s'aggira intorno ai cc. 0,3 e 0,4. Di questo eccesso parlano infatti anche i trattatisti† e Laurie‡ ha modificato il metodo al cromato di potassio per aumentarne appunto la sensibilità; invece del colore rosso del cromato di argento utilizza come reazione finale la colorazione gialla che il cromato di potassio aggiunto in eccesso comunica ad un leggero precipitato di cloruro di argento.

Condizioni d' esperienza.—Perchè una determinazione riesca veramente esatta impiegando come indicatore la difenilcarbazide, occorre usare alcune precauzioni. Alla soluzione di piombo, se acida per acidi minerali, si aggiunge tanto acetato d'ammonio da essere sicuri che non siano più presenti tali acidi allo stato libero; in ogni caso la soluzione deve essere acida per acido acetico. I prelevamenti del liquido precipitante è bene farli dopo alcuni minuti che si è aggiunto il cromato alcalino ed in non grande quantità in modo che la macchia resti limitata a non più di mezzo centimetro di raggio. Non si deve tener conto poi della colorazione che si forma sempre attorno alla periferia, anche quando si è in difetto di cromato. La colorazione invece con spiccata tendenza al viola, che dinota con molta sensibilità, essersi aggiunto, un leggero eccesso di liquido precipitante, si forma attorno al giallo del precipitato di cromato di piombo e compare fra i 30 o 40''.

Il precipitato di cromato di piombo non ha azione sulla cartina, però usando un pezzo di carta da filtro e facendo cadere le due gocce, una del liquido che si vuol saggiare e l' altra di difenilcarbazide in soluzione nell' acido acetico glaciale in modo che esse si intersechino

* Gazz. Chim. it. 26, i., 327 (1896).

† Fresenius L. c.

‡ Chem. News. lxviii., 211 (1893).

senza che il precipitato venga in contatto coll' indicatore, si arriva anche ad ottenere una maggior sensibilità.

1° cc. 29·00 di Pb $(NO_3)_2$ $\frac{N}{10}$, corrispondenti a gr. 0,3000 di Pb, richiesero cc. 29,00 di $K_2C_rO_4$ $\frac{N}{10}$

2° cc. 23·60 di Pb $(NO_3)_2$ $\frac{N}{10}$, corrispondenti a gr. 0,2441 di Pb, richiesero cc. 23,80 di $K_2C_rO_4$ $\frac{N}{10}$

3° cc. 14·20 di Pb $(NO_3)_2$ $\frac{N}{10}$ corrispondenti a gr. 0,1468 di Pb, richiesero cc. 14,25 di $K_2C_rO_4$ $\frac{N}{10}$

	Travato %			
	I.	II.	III.	Calcolato
Pb ...	62,51	63,04	62,75	62,51

3°—*Determinazione dell' acido solforico nei suoi sali.*—I primi tentativi per dosare l' ione SO_4'', vennero fatti aggiungendo alla soluzione del solfato un eccesso di soluzione titolata di nitrato di piombo e dosando l' eccesso di questo reattivo per mezzo del cromato di potassio. Questo metodo però non si presta affatto; in presenza del precipitato di solfato di piombo per ottenere la macchia sulla cartina si è dovuto aggiungere tanto cromato alcalino quanto occorreva per precipitare tutto il piombo aggiunto. Aggiungendo così a gr. 0,1710 di solfato di sodio cc. 29,50 di soluzione $\frac{n}{10}$ di nitrato di piombo, che porta ad un eccesso di cc. 5,1 di nitrato, si è dovuto aggiungere cc. 29,40 della soluzione equivalente di cromato potassico e ciò evidentemente per la reazione di doppio scambio fra il solfato di piombo ed il cromato di potassio:

$$Pb\,SO_4 + K_2C_rO_4 \rightleftarrows Pb\,C_rO_4 + K_2SO_4$$

reazione certamente reversible che in questo caso si compie in modo completo da sinistra verso destra per l'azione di massa del cromato alcalino.

Ho dovuto quindi introdurre nella determinazione dell' SO_4'' una filtrazione, precipitato l' SO_4'' con un eccesso di Pb $(NO_3)_2$ si filtra e nel filtrato si dosa l' eccesso di piombo per mezzo del cromato.

Quest' operazione non toglie però nulla di esattezza alla determinazione, e quando si precipiti il solfato di piombo a caldo e si riscaldi dopo fino all' ebullizione, il precipitato si deposita facilmente e non attraversa il filtro. Si può anche aggiungere alcune

goccie di acido cloridrico purchè si neutralizzi poi con acetato ammonico. Per la determinazione dell' eccesso di piombo mi sono messo naturalmente nelle stesse condizioni dette più avanti.

In quest' operazione ha grandissima importanza il lavaggio che fu fatto ripetutamente con acqua calda. Si possono saggiare le acque filtrate mediante la stessa soluzione titolata di cromato potassico tenendone conto nei calcoli finali ed aggiungendo le poche goccie di liquido raccolte in vetri da orologio alla parte principale del liquido filtrato.

1° gr. 0,2383 di Na_2SO_4, corrispondenti a gr. 0,1609 di SO_4'', richiesero cc. 33,40 di Pb $(NO_3)_2$ $\frac{N}{10}$

2° gr. 0,8696 di Na_2SO_4, corrispondenti a gr. 0,5874 di SO_4'', richiesero cc. 22,35 di Pb $(NO_3)_2$ $\frac{N}{10}$

	Trovato %		
	I.	II.	Calcolato.
SO_4''	67,26	67,53	67,55

Apparecchio per prendere il campione delle acque profonde.

Di A. Sanna.

Avendo avuto occasione di prendere campioni d' acqua a diverse profondità, mi sono servito di uno degli apparecchi più in uso, qual' è quello del Lepsius * :—

Questo strumento, com' è noto, a differenza degli altri, è formato in modo che il campione non viene a contatto coll' aria esterna e quindi è adatto per determinare con precisione i gas disciolti nell' acqua. Esso è formato da una scatola metallica in cui trovasi capovolto un pallone di vetro pieno di mercurio e turato da un tappo a doppia tubulatura. Uno dei tubi e affilato in punta capillare e chiuso alla fiamma. La punta capillare è collegata con una cordicella che si può tirare dall' alto. Con lo strappo di questa cordicella, la punta di vetro si rompe e allora cade il mercurio contenuto nel pallone, il quale per l' uscita di questo metallo si riempie d' acqua.

Ma non sempre con quest' apparecchio si riesce a fare il campione. Ricorderò che il più delle volte dopo la rottura della punta di vetro il mercurio non sgorga ; altre volte il vetro affilato oppone della resistenza e quando l' operatore dà lo strappo alla cordicella per rompere il tubo, questo trascina con sè il tappo. La bottiglia rimane così sturata e si riempie di acqua, ma, portata alla superficie, si vuota prima che l' operatore riesca a raccogliere il campione.

Con altri apparecchi s' incontrano meno inconvenienti, ma non si evita all' acqua presa a diverse profondità di venire a contatto con l' aria dell' atmosfera. Mi sono perciò servito di un apparecchio, che presento appunto perchè scevro delle difficoltà citate, non solo, ma mette l' operatore nelle condizioni di sapere se l' apparecchio ha toccato il fondo dell' ambiente in cui si trova l' acqua e se il recipiente di presa ha funzionato regolarmente.

Per comprendere l' importanza di questo fatto, bisogna mettersi nelle condizioni di fare il campione a diverse centinaia di metri di profondità.

Capita allora per le grandi pressioni che possiede l' abisso acqueo di credere di aver toccato fondo e quindi di estrarre il campione

* Nuova Enc. Ch. del Guareschi, vol. III., pag. 465.

da un' altezza diversa da quella voluta. C' è di piu ; tutti gli apparecchi di questo genere possiedono due corde, una per tenere legato lo strumento e l' altra per aprirlo onde dar addito all' entrata del l' acqua. Ebbene, il più delle volte le due corde s' intrecciano l' una coll' altra quando lo strumento gira su se stesso, e allora non è possibile fare il campione, dato l' attrito che oppongono fra loro le corde bagnate.

Il mio apparecchio * è costituito da un telaio metallico, pesante, formato da due aste che uniscono due anelli. Nell' anello inferiore è collocato un bicchiere (*a*), e in quello superiore (*o*) una bolla di vetro robusto (*b*), munito di due fori diametralmente opposti. Il foro superiore è chiuso da un turacciolo di ebanite (*c*) e quello inferiore da un tampone di vetro (*d*).

Tanto il turacciolo quanto il tampone hanno un movimento automatico e chiudono la bolla quando l' apparecchio è sospeso e *vice versa* l' aprono quando il telaio poggia per la base inferiore.

Il modo di operare è semplicissimo : la bolla riempita di mercurio viene collocata nel telaio appoggiata al proprio anello in modo che il tampone (*d*) non tocchi il piolo (*f*). Si abbassa l'asta che regge il turacciolo d'ebanite (*c*), sino a chiudere fortemente il foro superiore della bolla. Si sospende allora lo strumento alla corda di sostegno e si abbassa l' anello che sostiene la stessa bolla.

Puo capitare al momento che si abbassa l' anello (*o*), che il peso del mercurio impedisca all' operatore di tenere sospesa la bolla. Per evitare tale inconveniente ho collocato sul turacciolo di ebanite, un caviglio che dovrà togliersi dopo aver abbassato l' anello (*o*).

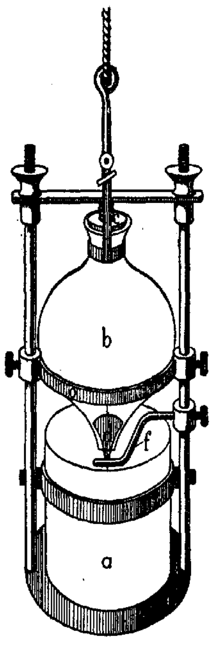
Tolto questo caviglio, l' apparecchio è pronto per essere immerso alla profondità voluta.

Quando lo strumento tocca il fondo dell' ambiente in cui viene immerso, il telaio si ferma e la bolla scorre ancora dentro lo stesso telaio sino ad appoggiarsi al proprio anello. In tal modo si apre superiormente (poichè il turacciolo è rigidamente unito allo stesso telaio) e va coll' estremità inferiore a toccare il piolo (*f*), il quale naturalmente solleva il tampone di vetro (*d*). Così il mercurio, per essersi aperti i due fori, fluisce dalla bolla, dando luogoall' en trata dell' acqua circostante.

* L'apparecchio è stato costruito dal Dottore Bosio e dalla Casa Zambelli.

Quando l' operatore tira la corda per sollevare l' apparecchio, la bolla si richiude portando seco il campione dell' acqua. L' operatore deve essere cauto di non posare l' apparecchio se non quando abbia di già mecsso il caviglio che sostiene la bolla, perchè questa non abbia a riaprirsi e perdere l' acqua contenutavi.

Per quando si opera a grande profondità, l'apparecchio è munito di una soneria elettrica che avvisa l' operatore al momento che lo



strumento tocca fondo. Intrecciati alla fune di sospensione vi sono due reoferi che finiscono in punte di platino comunicanti col l' interno della bola. Quando questa contiene mercurio, il circuito è chiuso e la soneria agisce; quando al contrario la bolla contiene acqua il circuito rimane interrotto e la soneria cessa di suonare.

Casale.

Gabinetto di Chimica dell' Istituto Tecnico.

Review of the Analytical Chemical Work of the several Bureaus of the U. S. Department of Agriculture and of the State Experiment Stations since 1903, except that on Foods and Drugs.

By W. W. Skinner.

The analytical problems occupying the attention of chemists of the U.S. Department of Agriculture and the several Agricultural Experiment Stations have continued along lines previously reported. Increased activity is to be noted in studies of plant production and soil fertility, while methods for the examination of food products have received considerable attention, due to the influence of the enactment of Federal and State food laws. The technical work of the Stations and Department of Agriculture has greatly increased in recent years.

Soils.

Comparison of methods for estimation of soil acidity, by F. P. Veitch (J. Am. Chem. Soc. 26, 637), is a discussion of the sodium chloride and lime-water methods. The lime-water method, first proposed by Veitch, has been modified and improved.

F. H. King (Proc. Soc. Prom. Agr. Sci., 1904, pp. 171) points out the importance from the standpoint of the relation of soil moisture to crop yields of a simultaneous study, which would reveal quantitatively and qualitatively the character of the solution which the soil moisture represents, both as it exists in the soil under the growing crop, and after it has been absorbed and becomes functional in plant growth. King and others (Wis. Sta. Rpt. 1902, pp. 339) also report studies on the development and distribution of nitrates and total water soluble salts in field soils.

Ladd and McGuigan (N.D. Sta. Rpt., 1902) report results of studies of composition and properties of humus from different sources, showing that when fractional precipitation is employed humus extracts greatly vary.

Schreiner and Brown (J. Am. Chem. Soc. 26, 1463) report a colorimetric method for estimation of phosphorus.

A comparison of Moore's method for estimation of potash with the A.O.A.C. method is made by Veitch (J. Am. Chem. Soc. 27, 56),

from which he concludes that the former is simple, accurate, and of wide applicability.

The determination of organic carbon in soils by a modification of Parr's method is reported by Pettitt and Schaub (J. Am. Chem. Soc. 26, 1640).

A method for the determination of black alkali in irrigating waters and soil extracts has been developed by Skinner (J. Am. Chem. Soc. 28, 78).

Selby and Ames (Ohio Sta. Bul., 150) give results of a very complete study of some Ohio soils, and discuss the significance of results in respect to the origin, geological relations, and general character of the soils. Studies of muck and peat soils is the subject of a report by Whitson and Stoddart (Wis. Sta. Rpt., 1904).

The nitrifying power of North Carolina soils has been studied by Withers and Fraps (N.C. Sta. Rpt., 1903), and they conclude that a soil with a low-water capacity, low absorption power, or low humus does not necessarily have a low nitrifying power. Investigations in soil fertility are reported by Whitney and Cameron (U.S. Dept. Agr. Soil Bul., 23), and observations on organic matter in soils. They conclude that no relation has been established between the movement of water, with its associated plant foods, and the fertility of soils. A centrifugal method of mechanical analysis of soils is reported by Briggs, Martin, and Pearce (U.S. Dept. Agr. Soil Bul. 24), to take the place of previous methods used. Copper salts in irrigating waters have been investigated by Skinner (J. Am. Chem. Soc. 28, 362), showing the extremely toxic nature of copper salts to vegetable life. Studies on the Properties of an Unproductive Soil, by Livingston, Britton, and Reid (U.S. Dept. Agr. Soil Bul. 28), is an investigation of the physiological properties of an extremely unproductive soil. It was shown that the water extract contained non-volatile substances toxic to wheat plants. The toxicity is corrected by certain agents, *i.e.*, tannic acid, pyrogallol, calcium carbonate, etc., some evidently acting chemically to neutralize the toxic bodies, others merely as absorbents. Certain organic constituents of soils in relation to soil fertility, by Schreiner, Reid, and Skinner (U.S. Dept. Agr. Soils Bul. 47), is a continuation of the investigation of the toxic bodies produced by growing plants. The action of water and aqueous solutions upon soil carbonates—Cameron and Bell (U.S. Dept. Agr. Soils Bul. 49)—is a study of the solubility of the hydrate and carbonates of lime, with special reference to its

application to the alkali problem of the arid regions. The effect of water on rock powders—Cushman (U.S. Dept. Agr. Chem. Bul. 92) —is a study of the behaviour of rock powders after being acted on by water, and it is shown that the formation of colloids upon the surfaces of the particles would account for the increased hardening power under the action of wet grinding.

Cameron and Bell (U.S. Dept. Agr. Soils Bul., 30) have studied the mineral constituents of soil solution, from which they conclude that the concentration of the soil solution with respect to the principal mineral plant food nutrients is sufficient for growth and development of crops. And further, the magnitude of the concentrations is the same for practically all soils. The development of modern soil chemistry is dependent upon a study of chemical changes induced by surface contact, and upon a study of the properties of water, soluble organic, as well as inorganic matter of the soil.

Schreiner and Failyer have compiled the colorimetric, turbidity, and titration methods used in soil investigations by the Bureau of Soils (U.S. Dept. Agr. Soils Bul. 31). The action of water and aqueous solutions upon soil phosphates is a study by Cameron and Bell (U.S. Dept. Agr. Soils Bul. 41), from which they conclude that the action of phosphate fertilizers is upon the soil, and not primarily upon the plant.

Calcium sulphate in aqueous solutions is a contribution to the study of alkali deposits by Cameron and Bell (U.S. Dept. Agr. Soils Bul. 33). The purpose of the bulletin has been to bring together and arrange in a logical sequence the results of numerous investigations which have been made on the relation of calcium sulphate to aqueous solutions.

A comparison of the organic matter in the different soil types is reported by Cameron (J. Am. Chem. Soc. 27, 256), and analyses of the organic matter in 1,340 samples of soil and 1,220 sub-soils are summarized.

Hilgard (Amer. J. Sci. 4, 1906) summarizes his observations regarding the phases of rock weathering and soil formation in arid regions, and concludes that there is need of caution in applying the maxims of humid regions in arid climates.

Peter and Averitt (Ky. Sta. Bul. 126) discuss the cause of unsatisfactory results in the determination of humus in soils, and propose a modification of the official method. The loss of nitrogen from soils is a study of the influence of methods of farming upon the nitrogen

content of soils by Snyder (Minn. Sta. Bul. 94). A chemical study of the lime and sulphur dip was made by Shaw (Tr. Kan. Acd. Sci. 20, 53). Paints and their composition—Ladd and Holly (N.D. Sta. Bul. 70)—is the subject of a treatise giving the analyses and methods of examining paints and pigments. E. C. Shory (U.S. Dept. Agr. O.E.S. Bul. 170) reports upon the acidity and nitrogen in Hawaiian soils. Cameron and Patten (J. Am. Chem. Soc. 28, 1639), report analyses and procolation tests in a study of the removal of black alkali by leaching. Maintaining the fertility of rice soils, Fraps (Tex. Sta. Bul. 82)—reports a study of the chemical composition and properties of rice soils, irrigating waters, and rice plants. The decomposition of feldspar—Cushmann and Hubbard (U.S. Dept. Agr. Roads Bul. 28)—deals with studies of mechanical, physical, and chemical factors, which modify the decomposition of feldspars. Ladd (N.D. St. Rept. 1904) reports the analyses of numerous samples of formaldehyde, and concludes that it is frequently adulterated.

MISCELLANEOUS.

H. Snyder (Minn. Bul. 85, pp. 179), in glutinous and starchy wheat, gives the analytical data, with special reference to protein content for comparing different grades of wheat.

A. J. Patten and E. B. Hart (N.Y. Sta. Bul. 250) have investigated the nature of the principal phosphorus compound of wheat bran. The free acid was prepared from the salt present in wheat bran, which, when treated with mineral acids, broke up quantitatively. The free acid corresponds to the formula $C_2H_8P_2O_9$, and is probably identical with Posternak's anhydro-oxymethylene-diphosphoric acid.

Woods and Merrill (Me. Sta. Bul. 103) report analyses of cleaned wheat and bran from entire wheat flour, and discuss the protein content of several grades of flour.

The relation of smelter smoke to Utah agriculture is the subject of a study by Widtsoe (Utah Sta. Bul. 88). Chemical examination showed the dust to contain a large quantity of iron, some copper, and traces of arsenic.

Parrott and Sirrine (N.Y. Sta. Bul. 254) report the value of sulphur washes for spraying. Kerosene and limoid mixtures: their chemical composition and use are described by Close (Del. Sta. Bul. 14).

Arsenic in paper and fabrics.—Haywood and Warner (U.S. Dept. Agr. Chem. Bul. 86) discuss the causes of poisoning by arsenical papers, and give methods used for determining arsenic in such

materials. Large amounts of arsenic were found in dress goods, furs, rugs, etc., and the danger of poisoning from such sources pointed out.

Haywood (U.S. Dept. Agr. Chem. Bul. 101) has investigated the lime-sulphur-salt wash, which is so largely used as an insecticide. The principal products from boiling the mixture for one hour were found to be calcium pentasulphide and calcium thiosulphate, and it is the slow decomposition of these products that gives to the product its excellent insecticidal properties.

Haywood and Smith (U.S. Dept. Agr. Chem. Bul. 91) have made a study of some of the prominent brands of mineral waters found upon American markets. With one exception, none of the so-called lithia waters examined were found to contain more than traces of lithium. Cassava, its content of hydrocyanic acid, starch, etc., is a study by Moore (U.S. Dept. Agr. Chem. 106).

Commercial feeding stuffs of the United States have been investigated by Haywood, Warner, and Howard (U.S. Dept. Agr. Chem. Bul. 108). Walker has studied some technical methods of testing supplies, including paint, paint materials, inks, oils, soaps, etc. (U.S. Dept. Agr. Bul. Chem. 109). Haywood (U.S. Dept. Agr. Chem. Bul. 113) has investigated the injury to vegetation and animal life produced by smelter wastes, and has shown that the sulphur dioxide and arsenic given off in smelter fumes is a serious menace to all agricultural operations in the vicinity of smelters; while the copper leachings seriously pollute the irrigation waters when allowed to run into streams.

The quality and adulteration of Sicilian Sumac has been investigated by Veitch (U.S. Dept. Agr. Chem. Bul. 117).

The commercial status of durum wheat in the United States is described by Carleton and Chamberlain (U.S. Dept. Agr. Ind. Bul. 70), and its value pointed out. The total proteid content of durum wheat is considerably higher than any of the principal classes of American wheats.

Sulphur washes for orchard treatment, Part II., by Parrott, Beach, and Sirrine (N.Y. Sta. Bul. 26) is a study of the applicability of sulphur washes as combined insecticides and fungicides.

The corrosion of iron has been investigated by Cushman (U.S. Dept. Agr. Roads Bul. 30), who discusses the carbonic acid, peroxide, and electrolytic theories, with experimental evidence against and in support of each. His opinion is that the electrolytic theory most satisfactorily explains the phenomenon of the corrosion of iron.

Some Amendments in the Kjeldahl Method for the determination of Nitrogen.

By JOHN SEBELIEN, *Aas, Norway.*

In spite of the undoubted advantages of this method, which makes it indispensable for agricultural and physiological researches, and in spite of the many improvements already in use with a view to shortening the boiling process with sulphuric acid, we consider that it is capable of still further improvement.

1. Boiling with sulphuric acid, in laboratories which have not a gas main pipe at their disposal, and where many of these analyses are being carried out at the same time, is inconvenient.

Some years ago, when we established our present laboratory of the Royal Norwegian Agricultural College, at Aas, I wished to make use of the electric current for heating the Kjeldahl flasks. I am glad to say that I persuaded Mr. W. C. Heräus, of Hanau, in Bavaria, to build an electric oven for this purpose. The heating space is formed like a cup, with an upper diameter of 11 cm. and a depth of 6½ cm.; it is lined with chamotte, in which the platinum resistance wires are enclosed. This cup can hold a round-bottomed Kjeldahl flask of 500 $cm.^3$ content, and of course ones of smaller size. The upper part of the heating-room is covered with a nickel cap, lined with asbestos, and fitted with a notch for the neck of the flask. The whole outside of the oven is made of bright sheet nickel.

In the event of a flask bursting, which seldom happens now that we use flasks of the best Jena glass, there is a loose nickel cup in the bottom of the cup-shaped heating space, from the lowest point of which a short tube leads the overflowing acid out of the oven.

The oven is directly connected with an electric installation, with a tension of 110 volts, and consumes 1·7 amperes. The temperature in the heating space will rise to about 200° C. in a quarter of an hour, and in about half an hour to 300° C. A temperature of 360° C. or more is obtained with more prolonged heating.

Therefore it is necessary when the boiling point of sulphuric acid is reached, or at the beginning of the process, when we only wish a gentle heat, to insert a resistance. This is most easily done when carrying out several analyses at the same time, and consequently we have a number of ovens placed near each other, working

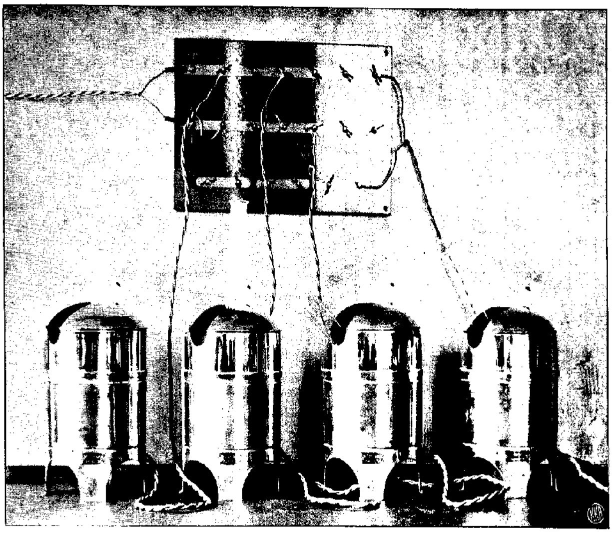


FIG. 1.

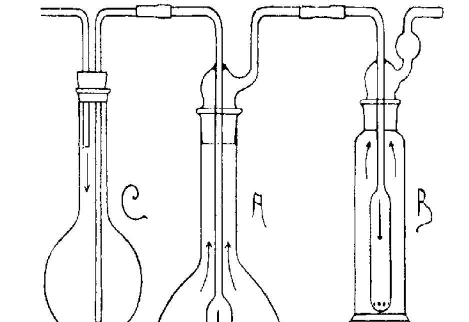


FIG. 2.

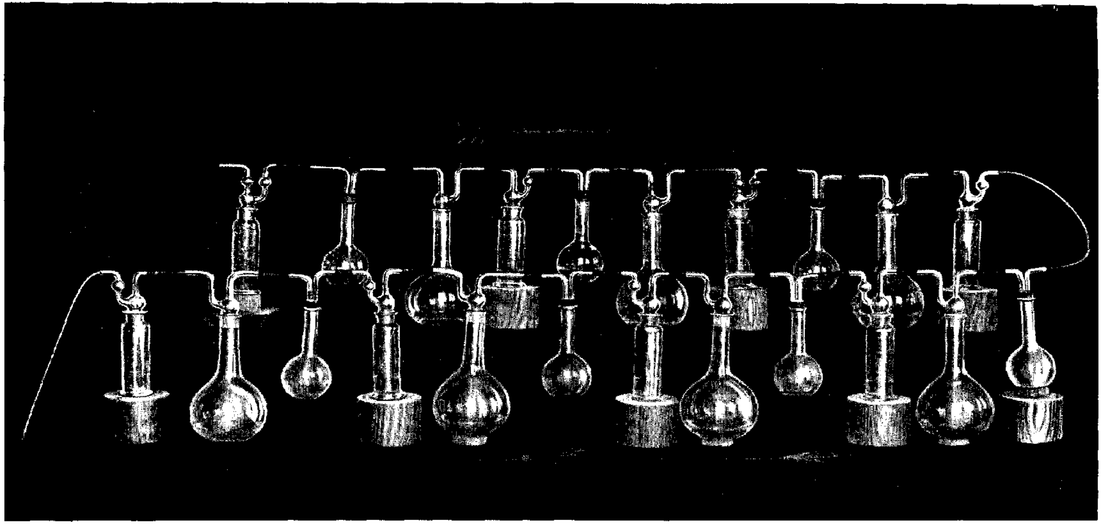


Fig. 3.

simultaneously. Then we connect the ovens so that one oven forms a resistance for the others. (Fig. 1.)

2. Distillation of ammonia may no doubt be carried out with great exactness in the ordinary way originally proposed by Kjeldahl,* but this method also gives rise to errors. First, there is the possibility of some of the ammonia just set free escaping through the alkaline solution before the distillation flask can be connected with the condenser.

It is well-known† that the glass tubes of the condenser are attached at no small extension of the heated ammoniacal fumes, especially when cold water is not used as a cooler.

We would draw attention to the bumping which often happens to the flasks during distillation, as well as to the large consumption of india-rubber stoppers, which soon wear out, and do not fit tightly into the necks of the distillation flasks.

We therefore propose to add the alkaline solution to set free the ammonia, so that no loss of it may occur, and to expel the free ammonia by a stream of air at ordinary temperature carried through the liquid.

For a long time experimenters have called attention to this method of expelling the free ammonia by means of a current of air. Folin,‡ notably, has used it to determine the amount of ammonia and carbonate of ammonia in urine. We find no reason to doubt why this method should not be applied to all determinations of ammonia, and also to the determination of the total, and the organic nitrogen.

We use (Fig. 2) a flat-bottomed glass washing bottle (A) of 700 $cm.^3$ capacity, with a hollow-ground glass stopper, having both inlet and outlet tubes. The inlet tube has an enlarged base, at the bottom of which there are a number of small holes, through which the current of gas passes, after having passed through the liquid. The outlet tube is fixed sideways in the upper part of the hollow stopper, and is bent in two places in order to prevent the spray from the liquid following the gas current.

The bottle A acts as a distillation bottle containing the liquid, together with the sulphate of ammonia produced by the boiling with sulphuric acid. The short horizontal branch of the inlet tube is

* Comptes Rendus du Laboratoire du Carlsberg, vol. II. Copenhagen, 1888.

† Pescheck. Journal für Landwirtschaft Bd. 57, 1906, p. 367.

‡ Zeitschrift für Physiologische Chemie, Bd. 37, p. 161, and Bd. 39, p. 477.

tightly connected with a small flask C, containing the alcalic solution. When the water air-pump begins to work, the solution is sucked from the flask C into the distillation bottle A, and frees the ammonia. When all the solution has passed into A, the current of air flowing in the direction indicated by the arrows in the figure, carries the free ammonia through the hollow-ground glass stopper into the absorption flask B, furnished with inlet and outlet tubes, as described above.

To purify the air current of atmospheric ammonia, a washing bottle containing strong sulphuric acid is placed at the left behind the bottle C.

The thoroughness with which the free ammonia is expelled depends upon the quantity of air passed through the solution. We found that for the expulsion of about 10 cc. $\frac{1}{5}$ normal ammonia, that is about 34 mgr. NH_3, a quantity of 200 to 250 litres of air is required. Using a Körting water air-pump, producing an air current of 70-100 litres per hour, the work takes about 2 hours. Folin uses a current of 700 litres of air per hour, and finishes his ammonia distillation in half an hour.

The speed of the analysis also depends on the degree of concentration of the hydrate of sodium and of the free ammonia in the solution—the greater these concentrations being, the more easily will the ammonia be expelled. Of course, any rise in the temperature will hasten the process, and the heat, generated by the neutralisation of the free sulphuric acid with hydroxyde of sodium will produce this result.

By separate experiments we have demonstrated that at the above-named strength of the air current, no spray from the alkali solution will be carried from flask A into the absorption vessel B, and no trace of the titrated acid in the latter will be carried away, just as every trace of ammonia will be absorbed by the acid in the absorption vessel B.

A great number of determinations may be carried out, not only at the same time, but by the same air current—the bottles being arranged in a series, as shown in figure 3. The cost of heating materials, gas, spirit, or benzene, is balanced by the cheaper cost of the water air-pump.

The process can be carried on day or night without the personal supervision of the analyst, and without any risk of the distillation flasks running dry or exploding.

A New Form of Laboratory Apparatus.

By J. W. Turrentine.

ABSTRACT.

Graphite has been found to be a satisfactory substitute for platinum in the construction of insoluble electrodes to be used in the usual sort of electro-chemical laboratory experiments. The graphite electrodes are cut from sheets of Acheson graphite, 0·5 cm. in thickness. They are 15 cm. × 2·5 cm. in dimensions. To one end of each, which previously has been electroplated with copper, a length of copper wire is soldered. By means of this, electrical connection is made with the electrodes. The graphite is heated, and is then treated with molten paraffin. This treatment not only does not impair the conductivity of the material and the nature of the deposit, but also prevents smutting by the graphite and the absorption into its pores of the aqueous solutions in which it is used.

As a substitute for the Classen platinum dish, used to such advantage in electro-chemical analyses and separations, a graphite cathode dish was constructed. It was turned out on a lathe from a 4 in. Acheson graphite electrode. In dimensions it is 9·5 cm. in diameter across the top, by 5 cm. in depth; its capacity is about 200 cc., and, when filled, it presents a cathode surface of about 50 square centimetres. The walls are thin, being only one millimetre in thickness, and the weight of the dish is about 35 grams. The treatment with paraffin to which it was subjected renders the dish so non-absorptive of aqueous solutions that even now, in its present stage of development, it may be used in the less accurate analytical electro-chemical processes. This fact is attested by results obtained in efficiency determinations made, in a preliminary way, by electrolysing a copper solution contained in the dish in series with a copper coulometer. These results agree as well with the standard as do those obtained with the platinum cathode dish. The cathode gain in the coulometer varied from that in the graphite dish by a maximum amount of 2 mg. When the platinum dish was substituted for the graphite one a similar deviation from the theoretical was observed. Further experiments are now being conducted, the object of which is to discover the methods of drying and other manipulations which will enable the graphite dish to be used in the more accurate electro-chemical analyses.

J. Wauters read a Paper

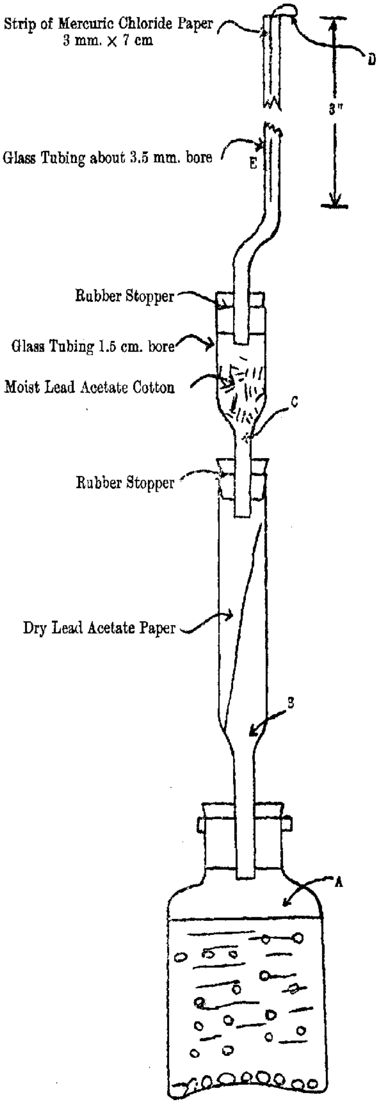
Sur une Réaction de la Saccharine.

Contributions from the Laboratories of the General Chemical Company of New York.

I.—The Determination of small amounts of Arsenic by the Gutzeit Method.

In the Journal of the Society of Chemical Industry of 15th November, 1907, there appeared an excellent article by Sanger and Black upon the determination of arsenic by the Gutzeit method. For more than a year this method, with certain modifications, which will be described later, has been in constant use in the laboratories of this Company. It has given such satisfaction that it has entirely superseded the Marsh-Berzèlius test. In case of manipulation, cost of materials, economy in time and in reliability, it is much to be preferred to the latter test, and has been found to be equally sensitive. The principle of the method is simple and well known: arsine is formed by the action of nascent hydrogen upon the arsenical compound, and the moist gas freed from hydrogen sulphide is allowed to pass along the surface of a strip of paper sensitized with mercuric chloride solution. A characteristic yellow brown stain is produced by the combination of the arsine with the mercuric chloride, and by comparing the length and intensity of this stain with a standard set of stains, the amount of arsenic is estimated.

(1) *Reduction Apparatus.* (See figure.)



The accompanying diagram shows the form and dimensions of the apparatus. (A) is a wide mouth bottle of about 60 c.c. capacity. Through a one-hole rubber stopper is inserted a glass tube (B) 9 cm. long and 1·5 cm. in diameter, constricted at the lower end so as to pass easily through the hole in the stopper. Through a stopper in the upper part of this tube is inserted a second similar tube of the same diameter, but only 5 cm. long. Finally, through a stopper in the upper tube is inserted a glass tube 3·5 mm. inside diameter, and 8 cm. long, bent as shown in sketch.

The lower glass tube is used as a scrubber to remove hydrogen sulphide from the arsine; for this purpose there is placed in the tube before each test a strip of dry lead acetate paper. The upper tube is packed loosely with cotton moistened with dilute lead acetate solution, and serves the double purpose of removing any traces of hydrogen sulphide which may pass (B), and of keeping the arsine saturated with moisture as it comes in contact with the sensitized test paper suspended in (E), a condition essential to the success of the test as clearly shown by Sanger and Black. J.S.C.I., 26, 1115-23.

(2) *Sensitized Test Paper.*

The above-mentioned authors advise the use of a 5 per cent. solution of recrystallized mercuric chloride as a sensitizer. It is to be noted, however, that the length of the stain produced from a given amount of arsine depends upon the strength of the mercuric chloride sensitizing solution, other conditions during the test being equal. By using a much weaker sensitizer, therefore, the sensitiveness of the paper is increased greatly. Very satisfactory results are obtained with a ½ per cent. solution of mercuric chloride. The paper used is Swedish filter paper No. 0 in square sheets 48 by 48 cm., and is sensitized and dried as described by Sanger and Black.* As soon as dry, the paper is cut into strips 7 cm. long and just wide enough to slip into the bent tube (E), discarding the ends of the sheets. A photographic print trimmer can be used to advantage in cutting the strips. The latter are immediately put into dry glass tubes, corked and sealed with paraffin until required for use. A large supply may be made up at one time and, if found necessary, a new set of standard stains prepared from every new lot of sensitized paper.

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* loc. cit.

(3) *Preparation and Preservation of Standard Stains.*

The set of standard stains is made of colour strips produced by 1, 2, 5, 10, 15, 20 and 25 micromilligrams of arsenic. The standard arsenic solutions used are prepared as follows:—1·32 grams of resublimed As_2O_3 is dissolved in a small quantity of sodium hydroxide solution (free from arsenic) acidified with sulphuric acid and made up to a litre with recently boiled water. To 10 c.c. of this solution in a casserole is added 2 c.c. nitric acid and a little sulphuric acid, and the solution evaporated on steam bath, until HNO_3 is all expelled. It is then diluted to a litre with boiled water. One c.c. of this solution (A) = ·01 mg. As. By diluting 100 c.c. of (A) to 1,000 c.c. with boiled water, solution (B) is obtained in which 1 c.c. = ·001 mg. As. These two solutions are all that are necessary in preparing the standard stains.

Copper-coated zinc and arsenic-free sulphuric acid (10 grams H_2SO_4 in 40 c.c. water) are used in the generating bottle, and the action allowed to continue for 30 minutes, when the test paper is withdrawn and immediately dipped in melted paraffin. The latter by filling up the pores of the paper slightly intensifies the stain and effectually protects it from the deleterious action of moisture. The set of stains when completed is mounted, side by side, on a white paper and the latter inserted within a test tube with the stains next the glass. A little P_2O_5 is first placed in the bottom of the tube, this is followed by a wad of ignited asbestos, and the set of stains rests on the latter. Finally the tube is sealed and kept in the dark when not in use. Such a set of stains prepared over a year ago has apparently not faded in the least, and has been in daily use during the whole of that period. There is therefore no necessity or advantage in "developing" the stains with HCl or NH_4OH, as employed by Sanger and Black (loc. cit.). With this ½ per cent. mercuric chloride sensitizing solution the colour stain for 1 mmg. As is a little longer than that produced by 2 mmg. As_2O_3 when the 5 per cent. solution is used, and the 25 mmg. stain equals that produced by 70 mmg. As_2O_3, as given on Plate 1, page 1123 (loc. cit.) Above 25 mmg. As the stains are too long to be accurate.

(4) *Making the Test.*

In the bottle (A) are placed about 15 pieces of copper-coated zinc.* In the dry tube (B) is placed a strip of lead acetate paper,

* About 1,000 grams Zn + 0·1 gram. $CuSO_4 \cdot 5H_2O$.

and the cotton in tube (C) moistened with dilute lead acetate solution before each test. The dried tube (E) is put in place and a strip of sensitized paper is suspended in it and held in place by bending the top of the paper over the edge of the tube. When all is in readiness the sample which should contain the equivalent of about 10 grams H_2SO_4 in a volume of 50 c.c. is poured rapidly into the bottle and the stopper with its connections inserted at once. Action should commence immediately and continue quite steadily for about thirty minutes, at the end of which time the paper is withdrawn from the tube, coated with melted paraffin, and compared with the standard stains.

Blank tests should of course be run frequently to ensure purity of reagents. The amount of zinc, acid and total volume in (A) should always be approximately the same, and the evolution of gas as nearly uniform as possible. Tube (E) is dried after each test.

Contrary to the experience of Sanger and Black, no appreciable difference has been found in the size of stain produced in 30 minutes when the arsenic is all in the oxidized state. Since, however, in the majority of samples tested the arsenic is in the oxidized form, it seems preferable to always oxidize before making the test if arsenious compounds are present, and to prepare the standard stains from a standard *arsenate* solution. If SO_2 is present it should be oxidized by addition of dilute $KMnO_4$ until the solution is faintly pink before making the test. In only rare instances has antimony been present in the samples analysed by this method. Since no appreciable stain is formed when less than 1 mg. Sb_2O_3 is present, no trouble has been experienced from this source.

Uniformity of conditions in the preparation of standards and in the running of actual tests is of course essential for accurate work.

II.—The Determination of minute quantities of Arsenic in Brimstone.

The minute quantity of arsenic usually present in Brimstone requires a very large sample to be taken for the determination. Oxidation of this large amount of sulphur is a difficult and tedious process. By substituting for the usual fuming nitric acid, a mixture of bromine and carbon tetrachloride, the oxidation is accomplished with comparative ease.

To 10 grams of the finely ground sample in a casserole are added 25 c.c. of a mixture of three parts by volume of carbon tetrachloride

to 2 of pure bromine. The casserole is covered with a watch glass and allowed to stand for 15 minutes. Nitric acid is then added, a few c.c. at a time until most of the bromine has been expelled, care being taken to prevent too violent evolution of the latter.

The casserole is then placed upon the steam bath and the nitric acid and carbon tetrachloride evaporated; the casserole is cooled, a few c.c. of water added, and again evaporated to expel the last trace of nitric acid. The sample is now ready for the determination of arsenic, which may be easily accomplished by the Marsh or Gutzeit method.

A blank determination should be made to prove the purity of the reagents.

The carbon tetrachloride dissolves the sulphur, which allows the bromine and nitric acid to oxidize the sulphur quite easily to sulphuric acid.

To arsenic-free sulphur were added small amounts of arsenic, and the latter determined as above, with the following results:—

Amount taken.	Amount found.
·01 mg. (=·0001 % As)	·008 mg.
·005 „ (·00005 „)	·005 „
·002 „ (·00002 „)	·002 „

III.—The Determination of Arsenic in Sulphuric Acid.

Introductory.

This method has been devised for the rapid determination of arsenic in sulphuric acid, when the arsenic content is too high for accurate estimation with the Marsh or Gutzeit apparatus (above ·002 per cent. As). It is especially valuable where economy of time is desired, since the whole analysis may be concluded within two hours.

The method is based upon the reduction of arsenic acid or its compounds to the arsenious condition, by tartaric acid, the expulsion of the excess of the latter by heat, and the subsequent titration of the arsenious acid with standard iodine solution. It is a modification of the method proposed by Mr. A. H. Low for the separation and determination of arsenic and antimony in ores. J. Am. Chem. Soc., 28, 1715 (Dec.).

Details of Manipulation.

Twenty-five c.c. of an acid containing about 0·1 per cent. As, or a larger volume in case the percentage is quite small, is measured into a short-necked Kjeldahl distilling flask. To the liquid is then added about half a gram of tartaric acid, and 2 grams of fused potassium bi-sulphate (free of arsenic). The flask is heated over a free flame, using an asbestos board with a hole of about 1½ inches in diameter. The sulphuric acid chars the excess of tartaric acid and the heating is continued until the solution becomes clear again, all the carbon being slowly oxidized. After cooling, the acid is poured into about 300 c.c. cold water, the excess acid nearly neutralised with ammonia, sodium bicarbonate added in excess, and the arsenious acid titrated with N/10 iodine, using starch and stopping only at the first permanent blue colour.

Remarks.

No loss of arsenic occurs through volatilization in absence of HCl. The small amount of ferric sulphate in commercial acid is not found reduced after this treatment. Antimony, if present, is reduced and titrated along with the arsenic. It is usually present in such small amounts as to be negligible. If, however, the acid contains an appreciable quantity of antimony, the iodine should be standardized against a similar sample of acid in which the percentage of arsenic has been carefully determined by the Pearce Silver Arsenate Method. (Cf. A. H. Low, Tech. Methods of Ore Anal., 1905, p. 44.) In this way the error arising from the antimony present is counterbalanced. It is easily possible to check within 0·1 c.c. iodine, and the results agree very closely with those obtained by the more tedious Pearce method.

Below are given a few comparative results between the tartaric and arsenate methods as determined in the same samples of acid:—

	Tartaric Method.	Silver Arsenate Method.
Arsenic ...	·096 %	·098 %
	·099 „	·098 „
	·090 „	·087 „
	·105 „	·105 „
	·167 „	·171 „

IV.—The Volumetric Determination of Sulphur in Pyrites Cinders.

A rapid method for the determination of sulphur in burnt pyrites is essential for proper works control. Such a method must be reasonably accurate when used for cinders of varying metallic composition and sulphur percentages. After a great deal of experimental work, preceded by careful trial of methods previously published, the following has been chosen. It has been in use for several months, and systematic checks made upon occasional samples by the gravimetric method have shown that it gives results well within the limits of accuracy required. The results obtained have proven much more satisfactory than those found by the alkalimetric methods of Pelouze (Compt. rend. LIII. 685; Zeit. f. Anal. Chem. I., 249) and of Watson (J.S.C.I. VII., 305). It is easily possible to determine the per cent. of sulphur in ten cinders within three hours from the time samples are received; this rapidity and its simplicity make it an exceedingly valuable method.

The method consists of two parts: (1)* Oxidation of the sulphur by heating with a mixture of sodium carbonate and zinc oxide, followed by, (2) extraction of the resulting sulphate with hot water, and titration with standard barium chloride in the presence of alcohol. An excess of barium chloride is always added and the excess titrated back with a standard solution of sodium carbonate.

Details of Manipulation.

(*a*) *Oxidation of the Sulphur.*

The cinders are finely ground and passed through a 100-mesh sieve, 1·5 grams are taken and intimately mixed with about 2 grams of "Soda-Zinc" (4 parts of zinc oxide to 1 part of sodium carbonate, both finely ground), transferred to a 30 c.c. porcelain crucible, and a thin layer of "Soda-Zinc" spread over the surface of the mixture. The crucible and contents are then heated over a Bunsen burner for 30 minutes, using full heat of the burner. The entire surface of the mixture should be a canary-yellow colour during the heating, the crucible being uncovered. The zinc oxide apparently acts as a carrier of oxygen, and the sulphur is converted to sodium sulphate without

* Cf. Ebaugh and Sprague. Use of Sodium Carbonate and Zinc Oxide in Sulphur and Arsenic determinations. (J. Am. Chem. Soc. 29, 1475-6 (Oct.).)

fusion of the mass. After heating, the crucible is cooled and its contents washed on to a 12½ c.c. No. 590 (S. & S.) filter. This is followed by six washings with boiling hot water, using not more than 15 c.c. for each washing. The completed extract should not contain more than 100 c.c.

(*b*) *Titration of the Sulphate.*

The colourless aqueous extract of the heated mass contains, besides sodium sulphate, some sodium carbonate. The CO_2 is removed by boiling with a small excess of dilute HCl (1 to 5). After cooling, 50 c.c of denatured alcohol* are mixed with the solution, and dilute NaOH (free from sulphate and carbonate) added from a burette until a very faint permanent pink is obtained, using phenolphthalein as indicator. 25 c.c. of standard barium chloride are run into this neutral solution changing the soluble sodium sulphate to insoluble barium sulphate. The excess $BaCl_2$ is then titrated with standard sodium carbonate solution until a permanent faint pink is secured. The presence of the alcohol makes the end point quite sharp. The calculation of sulphur percentage is simplified if the solutions are prepared as follows:—

(*c*) *Standard Sodium Carbonate.*

24·8 grams of c.p. 100 per cent. sodium carbonate (or its equivalent of soda of less strength) are dissolved in two litres of distilled water. Then 1 c.c. sodium carbonate solution = ·25 per cent. sulphur on 1·5 gram sample of cinder.

(*d*) *Standard Barium Chloride.*

100 grams of the crystallized salt are dissolved in water and diluted to four litres. This solution is standardized as follows:— To a beaker containing 100 c.c. distilled water and 50 c.c. denatured alcohol is added dilute NaOH until neutral to phenolphthalein. To this solution is added 25 c.c. standard $BaCl_2$ and the $BaCl_2$ titrated with standard Na_2CO_3 until the first permanent pink is reached. $\frac{\text{(c.c. } Na_2CO_3 \text{ required)}}{4}$ = value of 25 c.c. $BaCl_2$ in per cent. sulphur on 1·5 gram sample of cinder. A dividing burette holding 25 c.c. and connected with the four-litre reservoir of $BaCl_2$ can be used to advantage.

* 100 parts ethyl alcohol, 10 parts methyl alcohol, and ½ part benezin.

(*e*) *Calculation of per cent. Sulphur.*

The value of 25 c.c. $BaCl_2$ (as found above) minus $\frac{1}{4}$ the c.c. Na_2CO_3, used in the back titration equals per cent. sulphur in the cinder.

(*f*) *Modification of Method for Cinders very high or very low in Sulphur.*

If the cinder contains over 5 per cent. sulphur, 50 c.c. $BaCl_2$ should be used instead of 25 c.c. Should the cinder contain only a few tenths of a per cent. of sulphur, a 5 gram sample should be taken and the sulphur determined gravimetrically in the water extract. The volumetric method is not as accurate for such small amounts.

V.—Determination of SO_2 in dry Gases.

The ordinary Orsat apparatus in which the gases are measured over water and the absorbing pipettes contain aqueous caustic soda solution, cannot be used for the determination of SO_2 in dry roaster gases owing to the ready solubility of SO_2 in water. By substituting mercury for the water in the measuring burette and a solution of chromic acid dissolved in concentrated sulphuric acid containing about 85 per cent. H_2SO_4 or mixtures of concentrated sulphuric and phosphoric acids for the aqueous caustic soda in the absorbing pipette, this difficulty can be avoided. The aqueous vapour tension of such concentrated chromic-sulphuric-phosphoric acid mixtures is so small as to be negligible, and all the advantages of the Orsat of rapidity and convenience are thus available for the quick determination of SO_2 in dry gases for sulphuric or sulphurous acid manufacture.

VI.—Note upon Marsh and Gutzeit Tests.

In the determination of minute quantities of arsenic by either the Marsh or Gutzeit methods, one of the first essentials is to obtain a uniform reaction between the zinc and sulphuric acid. The ideal reaction is one in which the hydrogen is given off in very fine bubbles continuously during the whole of the test. Various methods have been proposed for accomplishing this result, and the most satisfactory one is the coating of shot zinc with a thin film of copper, using a half per cent. solution of copper sulphate as recommended by Lockemann.

From time to time it has been reported that this method failed to give satisfactory results, and quite recently in experiencing for the first time the same difficulty, we have endeavoured to ascertain the cause and apply a remedy. A qualitative test for impurities in the zinc showed it to contain a small trace of lead, and it was thought that this was responsible for causing the reaction to cease after about ten minutes.

It was recently shown in a paper read before the New York Section of the Society of Chemical Industry by Alexander, that a colloid added to a solution of lead prevents or delays the deposition of lead on zinc, and it was believed that if in this case the difficulty was due to lead coming down on the surface of the zinc, the addition of a small amount of gelatine or other colloidal solution would be advantageous. A solution of gum arabic (1 per cent.) was accordingly tried. It was found that 1 c.c. of this solution added to 50 c.c. of 20 per cent. sulphuric acid gave the desired reaction with the copper coated zinc. Since traces of lead are frequently present in arsenic-free zinc, it is believed that the above remedy will find a wide application.

VII.—Electrotitrimeter.

The electrotitrimeter was devised for determining accurately and quickly the H_2SO_4 content of sulphuric acid of high concentration, either in containers or in circulation. The previously great difficulties of applying electrical resistance methods for determination of strength in factory operations have been successfully met in this apparatus. The greatest source of error, due to changes in temperature, was overcome by the use of a compensating tube filled with acid of about the same strength as that to be tested, and permanently sealed. This tube and the test tube are kept at the same temperature by immersing in a bath consisting of the acid coming from the test tube itself, or in case of testing in containers, both tubes are lowered side by side into the acid.

The apparatus may be permanently set up and a small stream of the liquid passed through it continuously, or arranged in portable form and used as above described.

Patent rights in Canada have been secured and applications in the United States and European countries are pending.

The principal parts of the apparatus consist of a Wheatstone bridge, telephone receiver, pointer for determining the end point,

induction coil, dry battery, compensating tube, and tube containing liquid to be tested. By using long connections the bridge may be set up at a considerable distance from the testing tubes.

To make a reading it is only necessary to start the induction coil, place the telephone receiver to the ear and move the pointer along the bridge wire until the point of minimum sound is reached. The strength is then read off directly, the bridge wire having been previously so calibrated when standardized.

The sensitiveness of this method has been found to be approximately as follows:—

Oleum	30 % free SO_3	0·01 % Total SO_3
Sulphuric Acid...	100 %	0·01 „ H_2SO_4
„ ...	99 „	0·03 „ „
„ ..	98 „	0·05 „ „
„ ...	97 „	0·15 „ „
Free HCl in Bichloride of Tin ...		0·04 „ HCl

This last is only slightly affected by change of 1° Bé in the strength of the solution.

It is also applicable for testing water, solutions of various salts and alkalies.

By this simple apparatus an unskilled labourer in a few seconds' time secures results generally closer to the truth than those obtained by refined volumetric methods in the hands of a skilled analyst.

Analyzed Chemicals.

By J. T. Baker.

"Analyzed Chemicals" represent one of the latest efforts on the part of the manufacturing chemist to furnish the analytical chemist with chemical reagents of the highest degree of purity attainable under conditions limited by skill and economy, and labelled in a manner which can be intelligently understood. The common method of designating a chemical as "C. P." has resulted in much confusion owing to the fact that "chemically pure," strictly speaking, is impracticable. A chemical accompanied with a statement of analysis affords both a standard of purity, and, at the same time, a

guarantee of quality. The analysis states in definite terms the highest degree of purity attained, and is in itself a guarantee in regard to which there can be no misunderstanding. It also shows the amount of impurity present calculated in percentage from samples large enough to obtain a determinable amount. Although the amount of impurity present, as shown by the analysis, may be insignificant, it is satisfactory to know it, and affords an assurance which cannot be obtained in any other way. The object aimed at is to get away as far as possible from the errors of "personal equation" by getting results down to a mathematical basis.

Laboratory Chemicals.

By G. P. Adamson, *Easton, Pa.*

The testing of chemicals shows the lack of a universal standard method for general use. The present terms to designate the quality of chemicals are misleading. The word pure should be sufficient to distinguish between technical and purest grade. The great difficulty is in obtaining, on a manufacturing scale, a chemical which is chemically pure, owing to the apparatus that must be employed and the impurities in the air, water, and apparatus, which are not taken into consideration in technical chemicals. Many instances are cited to show the impossibility of a true chemically pure chemical, and the reasons given why they cannot be produced excepting at a prohibitive price and in small quantities. The factors entering into the analysis are: size of sample, method of sampling, and personal factor (the operator), the solubility of precipitates in solutions, and the solubility of apparatus. All analysis should be made under the actual working conditions and "blank determinations" should be made. Where the impurities are in minute quantities, colorimetric or volumetric methods should be used. All methods used should be universal standards.

Compte-rendu des travaux de la Commission Internationale d'Analyses, au VII^me Congrès international de Chimie appliquée,

par M. L. LINDET.

GRÂCE au zêle de mes collègues de la Commission international des analyses, j'ai pu réunir, faire imprimer et distribuer, avant la réunion du Congrès, les rapports des différentes Sous-commissions, et il résulte de l'examen qui en a été fait que les Sous-commissions suivantes peuvent être considérées comme ayant terminé leurs travaux :

Sous-Commission I (M. Chesneau, président) : Méthode unitaire pour le dosage du zinc dans les minerais ;

Sous-Commission III (M. Weinstein, président) : Graduation des appareils destinés à l'analyse volumétrique et gazométrique et des aréomètres ;

Sous-Commission VIII (M. Meunier, président) : Analyse qualitative et quantitative des matières tannantes ;—Unification des méthodes d'analyse des jaunes d'œufs ;

Sous-Commission IX (M. Lewkowitsch, président) : Détermination du titre des suifs et dosage du non-suif ;—Recherche des huiles de poissons dans les huiles industrielles ;—Distinction des huiles de pétrole et des hydrocarbures provenant de la décomposition du suint ;

Sous-Commission XI (M. Menozzi, président) : Unification des méthodes d'analyse des tartres.

Des notes additionnelles de M. Nissenson, de M. Weinstein, de M. Halphen, et de M. Menozzi seront publiées par mes soins dans le plus bref délai.

D'autre part la Commission a adopté à l'unanimité les conclusions de la Sous-Commission II (présidée par M. Wilhelm Fresenius) (Préparation uniforme des réactifs), de la Sous-Commission VII, présidée par M. Zacharias (Dosage de la laine, de la soie et du coton dans les tissus mélangés, et de la soie artificielle dans les passementeries) ; mais elle a jugé, d'accord avec les présidents intéressés, que ces Commissions devaient continuer leurs travaux.

Il en est de même de la Sous-Commission IV, présidée par

M. Wiley (Échantillonage des produits soumis à l'analyse), dont les résultats n'ont pu parvenir assez à temps pour que je puisse les faire imprimer et que la Commission puisse les discuter.

La Commission a en outre approuvé les conclusions de la Sous-Commission V, présidée par M. Sebelien (Unification des méthodes d'analyse de la cellulose); mais elle les a restreint au dosage de la cellulose dans le bois. Une nouvelle méthode doit être recherchée pour le dosage de la cellulose dans les celluloses purifiées telles que la pâte à papier.

Elle a enfin adopté les conclusions de la Sous-Commission VI, présidée par M. Heinrich Fresenius, relatives à la représentation des résultats d'analyse des eaux minérales, et a admis, avec M. Chesneau, que dans le cas des analyses courantes, le chimiste pourrait recourir à une représentation simplifiée des résultats. La Commission continuera sous la présidence de M. H. Fresenius à étudier d'autres questions relatives à la représentation des résultats d'analyse.

Comme vous le voyez, Messieurs, si nous devons nous féliciter des résultats acquis, nous devons également nous préoccuper de l'avenir. D'autres questions nous ont été posées, ou nous serons posées, et nous demandons au comité de Londres, ce que mon prédécesseur, le Dr. Lunge, a obtenu du comité de Rome, de nous aider pécuniairement, pour nous permettre de continuer ces travaux.